DISPOSAL OF OILFIELD WASTES BY LANDTREATMENT: EFFECTS ON THE ENVIRONMENT AND IMPLICATIONS FOR FUTURE LAND USE, 1987 RESEARCH PROJECT

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R.M. Danielson, N. Okazawa
Kananaskis Centre for Environmental Research
The University of Calgary

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W.J. Ceroici
Groundwater Protection Branch
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A report prepared for
The Canadian Petroleum Association
and
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June 1988

CANADIAN PETROLEUM ASSOCIATION

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EXECUTIVE SUMMARY

Landtreatment sites at Drayton Valley, Grande Prairie, and Brooks which had been planted to perennial crops in 1986 were visually assessed for plant growth. At Grande Prairie and Brooks growth was generally poor in the first year but improved substantially in the second year. Crop development appeared to be more limited by initial establishment than by current oil levels in the soil. At Drayton Valley, timothy and red fescue produced good crops on most plots in both 1986 and 1987. The site at Lloydminster was cultivated and replanted to barley in 1987, with the adjacent field serving as a control.

Growth at Lloydminster was very similar to that observed in 1986 with only poor to fair growth occurring on most sludge-treated plots. Soluble salts were moderately high in most plots although some plots had apparently received relatively low quantities of salts when the sludge was applied. The soil pH ranged from 7.0 to 7.7, electrical conductivity from 1.4 to 4.3 ds m^{-1} and sodium absorption ratio from 2.0 to 7.1. Total carbon in the treated plots was about three-fold greater than in the control soil. Soluble salts were higher in the surface 0-2 cm of soil than in the bulk soil with values as high as 11 ds m^{-1} being recorded. Heavy metals in the soil and plant tissues were not excessive and do not appear to pose any environmental threats.

In the greenhouse,barley grew moderately well in soils that supported only poor growth in the field. However, barley in all sludge-treated soils was chlorotic, perhaps indicating the decomposer organisms were rendering soil nitrogen unavailable. Clover grew more poorly than barley and was more sensitive to oil and/or salts in the soil.

The oil content decreased in all 16 of the Lloydminster plots with decreases ranging from 3 to 28% with an average decrease of 15%. At the end of 1987, total oil content of the soil ranged from 2.1 to 7.0%. At current rates of degradation, full productivity would not be achieved for 5 to 10 years in the most heavily treated plots. The

asphaltene fraction of the extracted oil generally increased between 1986 and 1987, with an overall average increase of 10%. However, the asphaltenes were being degraded as the total asphaltene content of the soil decreased by 11%.

Procedures were refined for extracting organic compounds from plants grown on sludge-treated soils to evaluate the potential risks of using crops from these soils. Comparisons were made of straw and grain from heavily treated soils and of the control soil. A tracer study indicated that the method recovered high percentages of the target compounds. GC/MS analyses of the barley extracts showed some differences (qualitative as well as quantitative) betweem the two sets of plants. The straw grown on oil-treated soil revealed a few unusual heterocyclic compounds which were not apparent in the control samples. Naturally-occurring fatty acids were the predominant components of all the extracts; however, some of these were either overproduced or not produced at all in the unhealthy plants from the oily soil.

Chemical degradation of the asphaltenes from Plot 6E was undertaken in an attempt to pinpoint potentially hazardous compounds which may eventually be released from the asphaltene structure as the biodegradation slowly progresses. Aromatic species which were chemically liberated from the asphaltenes were identified by GC/MS, and could be grouped into eight categories. These included carbazoles, benzofurans, naphthalenes, benzothiophenes, naphthols, flav-3-enes, disulphides and thianthrenes. However, only a small fraction of the asphaltene structure was studied and thus the long term potential hazard of asphaltene degradation products cannot be conclusively evaluated.

Both oil contents and salt concentrations in the soil appeared to have adverse effects on plant growth. Below 3% total oil content, plant growth was good unless salt concentrations, expressed as electrical conductivity of saturated extracts, exceeded 3 ds m^{-1}. Moderately good growth occurred even with an oil content of nearly 5% when the electrical conductivity was 1.6 ds m^{-1}. In terms of total

asphaltene content in the soil, good growth occurred below 0.6%, fair growth between 0.6 and 0.96%, and poor growth above 0.96%.

For groundwater studies, fifteen piezometers and seven water table wells were installed. The plots are underlain by relatively low permeability silty clay to a depth of at least 9 m. Fractures were detected in the till to a depth of 2.5 m. The predominant direction of shallow groundwater flow is to the east-northeast, and depth to water table averaged 2.5 m. Shallow groundwater is contaminated with chlorides but concentrations decreased rapidly with depth. The surface water is also contaminated with chloride, nitrate, and sulphate.

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1. INTRODUCTION

Landtreatment sites were established near Lloydminster, Grande Prairie, and Drayton Valley in 1982, and near Brooks in 1983 in order to study the feasibility of using this technique for the disposal of oil field wastes in Alberta. A variety of rates and types of oily wastes were applied in 1982 through 1985 in combination with cultivation and fertilization treatments (Figure 1). These field studies established that degradation of the wastes occurred but that large amounts of hydrocarbons remained in the soil (Peake et al. 1985, Peake and Connery 1986).

In 1986 the emphasis of the research shifted to rehabilitation of sites and assessments of soil productivity, crop quality, and water contamination (Danielson et al. 1987). The 1986 studies were summarized by Danielson et al. (1987) as follows.

The site at Lloydminster received the most intensive study followed by Drayton Valley. The sites at Grande Prairie and Brooks were given the lowest priority. All the four sites were planted in June 1986 with crops appropriate to each area; barley at Lloydminster, hay at Drayton Valley and Grande Prairie, and dryland pasture species at Brooks. Plant growth in all treatments at all sites were assessed visually in the fall and limited quantitative assessments were done at Lloydminster and Drayton Valley.

Growth of barley at Lloydminster ranged from poor to excellent but did not strictly reflect the amounts of oily wastes that had been applied to the plots. Growth did not appear to be influenced by past cultivation or fertilization treatments. Growth of hay at Drayton Valley ranged from poor to good and appeared to conform to the pattern of sludge application. Plant growth at both Grande Prairie and Brooks was poor to fair.

Soil analysis at Lloydminster did not reveal large differences among sludge treatments with the exception of salt content. It appeared that Cl levels may have been high enough to adversely affect the growth of barley in some treatments. Salt concentrations were much lower at Drayton Valley and posed no problems to rehabitation of that site.

When barley and alfalfa were grown in soils taken from the four sites and placed in the greenhouse, somewhat different patterns of

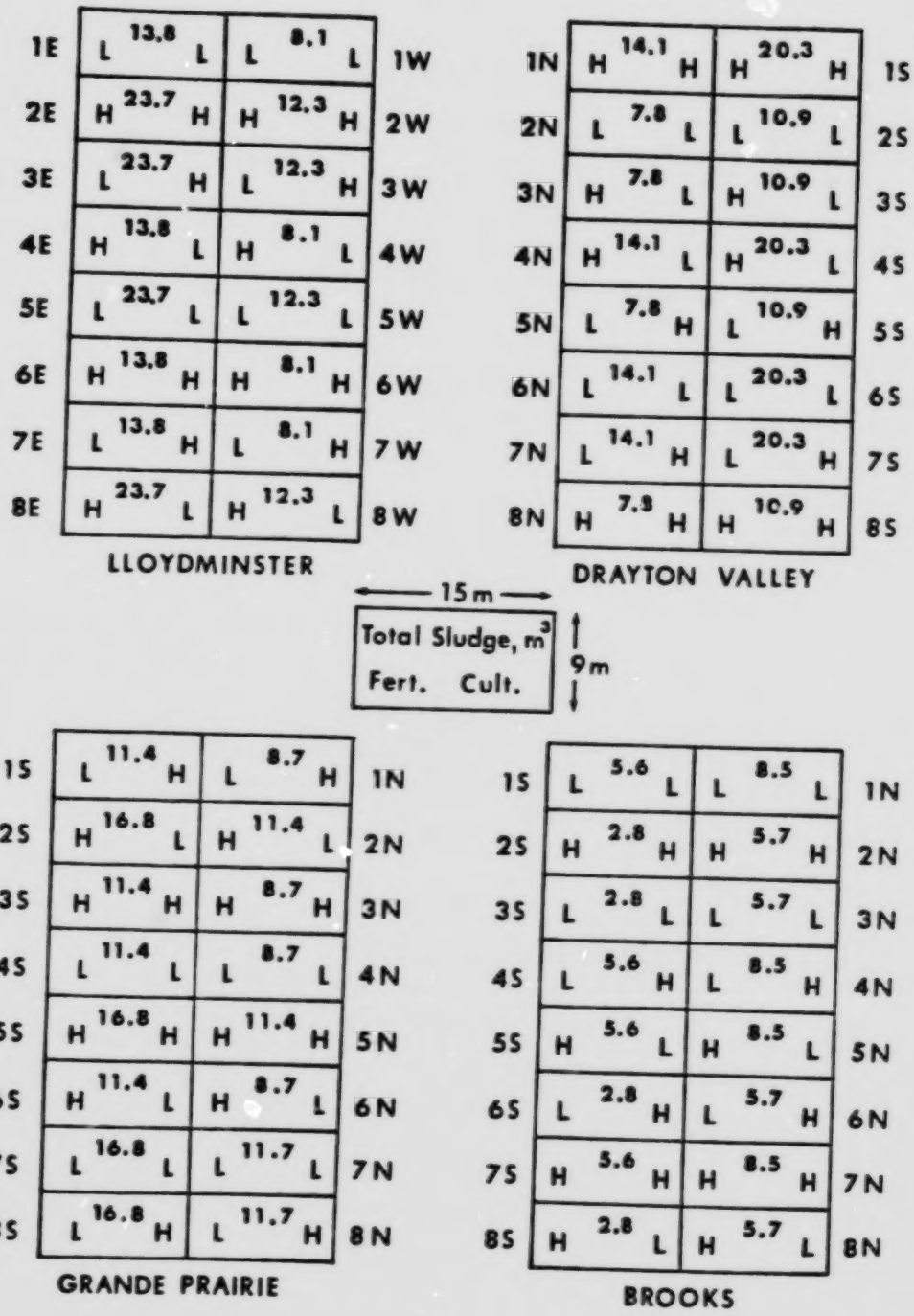

1E L 13.8 L L 8.1 L 1W
2E H 23.7 H H 12.3 H 2W
3E L 23.7 H L 12.3 H 3W
4E H 13.8 L H 8.1 L 4W
5E L 23.7 L L 12.3 L 5W
6E H 13.8 H H 8.1 H 6W
7E L 13.8 H L 8.1 H 7W
8E H 23.7 L H 12.3 L 8W
LLOYDMINSTER
1N H 14.1 H H 20.3 H 1S
2N L 7.8 L L 10.9 L 2S
3N H 7.8 L H 10.9 L 3S
4N H 14.1 L H 20.3 L 4S
5N L 7.8 H L 10.9 H 5S
6N L 14.1 L L 20.3 L 6S
7N L 14.1 H L 20.3 H 7S
8N H 7.8 H H 10.9 H 8S
DRAYTON VALLEY
15 m
Total Sludge, m3
Fert. Cult.
9m
1S L 11.4 H L 8.7 H 1N
2S H 16.8 L H 11.4 L 2N
3S H 11.4 H H 8.7 H 3N
4S L 11.4 L L 8.7 L 4N
5S H 16.8 H H 11.4 H 5N
6S H 11.4 L H 8.7 L 6N
7S L 16.8 L L 11.7 L 7N
8S L 16.8 H L 11.7 H 8N
GRANDE PRAIRIE
1S L 5.6 L L 8.5 L 1N
2S H 2.8 H H 5.7 H 2N
3S L 2.8 L L 5.7 L 3N
4S L 5.6 H L 8.5 H 4N
5S H 5.6 L H 8.5 L 5N
6S L 2.8 H L 5.7 H 6N
7S H 5.6 H H 8.5 H 7N
8S H 2.8 L H 5.7 L 8N
BROOKS

Figure 1. Plot arrangement and treatments of oily sludge, fertilizer, and cultivation at the four landtreatment site, 1982-1985.

growth were observed. Barley grew moderately well in all the soil treatments even though growth had been poor in the field in some cases. In contrast, alfalfa was more sensitive to chemical stresses and mirrored results obtained in the field.

Although the pattern of barley growth at Lloydminster was not predictable from the sludge application rates, except in extreme treatments, the residual oil in the soil was a valuable parameter in evaluating crop growth. Average values ranged from 2.6 to 8.6%. Good growth of barley usually occurred when the oil content was 3.5% or lower and was invariably poor when the oil content exceeded 5%. The best growth occurred when both salt and oil concentrations were both relatively low. Similar oil content-plant growth relationships were found at Drayton Valley as good growth occurred when the oil content was below 3% and was poor when it exceeded 4%.

Oily sludge decomposition has proceeded at uneven rates in the Lloydminster plots as plots that had similar amounts of sludges applied in the past contained quite different quantities in 1986 and visa versa. The causes for the different rates of decomposition were not apparent but it appeared that moderately large amounts of sludge could be applied and the sites returned to agriculture in a relatively brief time.

The chemical composition of the residual oil at Lloydminster was determined to be 15-18% asphaltenes, 22-25% resin 1, 21-25% resin 2, 16-23% aliphatics, and 11-16% aromatics. Attempts to further resolve the chemical nature of the aromatic fraction was unsuccessful. The asphaltenes did not appear to be accumulating in the soil even though this fraction is one of the least biogradable ones.

Straw from two plots at Lloydminster was analysed for uptake of aromatic hydrocarbons that could adversely affect the use of crops grown on oil-treated soils. Results of the analysis did not indicate that any uptake and retention had occurred, however the analytical techniques required further refinements before definite conclusions concerning plant uptake of undesirable chemicals could be reached.

Groundwater wells and piezometers were installed on the Lloydminster site to determine surficial geology, monitor groundwater flow patterns, groundwater depths, and possible contamination of the

groundwater. The plots are underlain by relatively low permeability silty clay till to a depth of at least 9 m. Fractures were detected in the till to a depth of about 2.5 m. The predominant direction of shallow groundwater flow was to the east-northeast. Shallow groundwater beneath and down gradient from the plots was contaminated, primarily with inorganic constituents, especially chloride and nitrate, and possibly lead. The contamination of chloride decreased rapidly with depth. Surface water was contaminated with chloride, nitrate, and sulphate.

2. OBJECTIVES

1. To further assess soil productivity quantitatively at Lloydminster and qualitatively at Brooks, Grande Prairie, and Drayton Valley.
2. To determine the critical oil content in the soil, below which crop growth is similar to untreated soil.
3. To determine if Cl is limiting crop growth at Lloydminster.
4. To determine if crops at Lloydminster contain undesirable organic compounds or heavy metals.
5. To determine if the oily wastes applied at Lloydminster have continued to degrade in the 1986-1987 period.
6. To monitor groundwater and surface water at Lloydminster for organic and inorganic contaminants.
7. To degrade asphaltenes from Lloydminster and conduct an analysis for potentially mobile organic compounds.

3. PLANTING AND SAMPLING FIELD PLOTS

3.1 PLANTING

The sites at Drayton Valley, Grande Prairie and Brooks were planted in 1986 with perennial crops (Table 1) and no further cultural practices were applied. In May of 1987, the study area at Lloydminster was cultivated and planted with Leduc variety barley and fertilized with 39 kg 46:0:0 and 20 kg 11:51:0. The surrounding field, which served as the control area was planted on the same day with seed from the same lot and fertilized similarily. Soil moisture was favourable and early growth of the barley was good. The surface runoff pond was pumped out in early June to prevent flooding of the central plots in the event of heavy precipitation. Weeds were cut around the plots in early June and, due to an error, the crops in plots 1, 2, and 3 were also cut at that time.

3.2 PLANT AND SOIL SAMPLING

Visual estimates of plant growth were made at all four sites as was done in 1986 (Danielson et al. 1987). Quantative estimates of the growth of barley at Lloydminster was also done in 1987 as in 1986 by harvesting five preselected 1 m^2 clip plots in each treatment plot. Five addition clip plots were taken from the adjacent field to serve as controls. The samples were air-dried and the gain and straw eighted separately. In addition to the 80 samples from the preselected points and the five control samples, growth was also assessed on five 1 m^2 quadrats transecting the northern end of plots 8E and 8W on which there was a gradient in plant growth from poor to good.

Soils were sampled on October 2, 1987 from the same preselected points that were used for plant sampling in 1986 and 1987. Five samples from the 0-10 cm depth were removed with a shovel or trowel from each 1 m^2 quadrat and composited (i.e., five composite samples from each treatment). The samples taken included the following:

a) samples from all treatments (16 plots, control and 8EW transect; 90 total) for oil content and soluble salts (~1.5 kg/sample);

Table 1. Planting of landtreatment sites in 1986 and 1987.

Site[1] (Planting Date)	Cultivation	Fertilizer	Seed
Lloydminster (March 14, 1987)	Rototilled	39 kg 46:0:0 20 kg 11:51:0	Leduc barley
Drayton Valley (June 10, 1986)	Harrowing	16-20-0 34-0-0 50 kg/ha each	30% Creeping red fescue 30% Richmond timothy 20% Alsike clover 20% Meadow foxtail 15 kg/ha
Grande Prairie (June 17, 1986)	Harrowing	12-15-0 50 kg/ha	10 lb alfalfa 4 lb timothy Total used
Brooks (June 18, 1986)	Harrowing	11-51-0 34-0-0 50 + 25 kg Total used	40% Crested wheatgrass 40% Russian wild rye 20% Sainfoin 50 kg used

1 All of site areas at Lloydminster, Grande Prairie, and Brooks, including borders were cultivated and planted. Plots 24,000 ft^2 (2230 m^2), borders approximately 7000 ft^2 (650 m^2). Only the plot area at Drayton Valley was planted.

b) samples of the eight west plots for a greenhouse growth study of clover and barley (eight plots and control, 45 samples, 3-5 kg/sample);

c) surface (0-2 cm) samples for soluble salts in plots 5W, 7W, and 8W (15 samples, 1.5 kg/sample). These samples were taken as salt deposits were observed on the soil surface where growth was poor but were largely absent where growth was fair to good. In addition, root growth appeared to be limited to the surface layer where growth was poor. Analysis of these samples should indicate if salt concentrations are higher near the soil surface than in the bulk soil and could be critical in plant establishment; and

d) samples of plot 6E for asphaltene composition (5 samples, 2-3 kg/sample).

All samples were sieved through a 4 mm sieve and all oily clods broken up and incorporated into the samples. Samples for organic analyses were further sieved through a 2 mm sieve as was done in 1986.

4. OIL CONTENT, CHEMICAL ANALYSES, AND PLANT UPTAKE

4.1 OBJECTIVES

The effectiveness of biodegradation as a means of disposal of oily wastes can be evaluated by following the changes in oil content of the soil as time elapses. Measurement of oil degradation at the four experimental landtreatment sites was undertaken for 3 years (from 1982 to 1984), with only the Lloydminster site being examined in 1985. In 1986, the determination of oil content was confined to the Lloydminster and selected plots of the Drayton Valley sites. The objective of the present study was to narrow the focus somewhat, and to concentrate on monitoring the disappearance of oil only at the Lloydminster site.

Concern exists over the eventual release of harmful mobile organic compounds as the biodegradation of the oil progresses. Once such water-soluble components are no longer bound within a complex, high molecular weight structure, they may pose a threat to groundwater contamination and/or uptake by plants. A second objective, therefore, was to attempt to mimic, by chemical means, the biodegradation process on the fraction of the oil most likely to liberate potentially deleterious organics, and to establish the identities of any mobile constituents.

It follows naturally that crops grown on oil-treated soil require extensive examination to assess possible dangers from consumption. The sites were planted for the first time in 1986, but initial investigations were hampered by the lack of an adequate method of analysis. A third objective was to improve upon the previously used extraction procedure and to test its effectiveness through the use of tracers. Once the procedure proved satisfactory, it would then be applied to freshly-harvested plant material. Comparisons with crops grown on untreated soil would reveal the existence of any extraneous organic substances. Once their identities are known, possible hazards related to their presence in the crops can be better understood.

4.2 MATERIALS AND METHODS

4.2.1 Sample Preparation

4.2.1.1 Soil samples. All soil samples were processed through a 2 mm sieve. Aggregates too large to pass through were transferred to a mortar where they were crushed. Stones and pieces of plant material were removed by hand. Sieved samples were packaged in fresh plastic bags and stored under refrigeration.

4.2.1.2 Plant samples. Plant samples were sorted into respective grain and straw portions. The husks were removed by hand from the grain and any roots or weeds eliminated from the stems and leaves. Samples were then individually rinsed in distilled water and allowed to air dry at ambient temperature. Once dried, they were processed through a Wiley mill (with mesh size 40).

4.2.2. Sample Treatment

4.2.2.1 Procedure for oil content analysis. Each (20.0 g) of the 80 soil samples from the Lloydminster site was extracted with toluene (ca. 200 mL) for 3-4 hours in a conventional Soxhlet apparatus incorporating a Dean-Stark trap to separately collect water. The freshly extracted soil was dried in a vacuum oven at 45°C for approximately 1 day to ensure the removal of residual toluene. This procedure produces a soil which is free of water and sources of organic carbon, and is necessary for the subsequent determination of the oil content. The extracted oil, still dissolved in toluene, was used for the subsequent asphaltene measurement (see Section 4.2.2.2).

4.2.2.2 Procedure for asphaltene precipitation. Asphaltene contents were measured for all 16 subplots of the Lloydminster site. The oil for the asphaltene determination was acquired in a slightly different manner than in the previous year. Rather than preparing 16 samples containing equal proportions of soil from the 5 subsamples within each subplot and extracting each composite sample, this year the oil

extracted for the oil content analysis was used (see Section 4.2.2.1). Since equal weights of soils were extracted, the 5 extracts from each subplot could be combined to provide an average sample. From this stage onwards, the usual procedure was followed. The toluene remaining from the Soxhlet extraction was removed by rotary evaporation, and a constant weight was established. The resultant oil was then redissolved in toluene (1 g oil:1 mL toluene) and a twenty-fold excess of hexane was added. The asphaltenes were allowed a minimum of 3 hours to settle before being collected in a glass filtering funnel under vacuum. Once dried, a weight could be obtained and the corresponding percentage of asphaltenes in the oil calculated.

4.2.2.3 Procedure for chemical degradation.

4.2.2.3.1 Extraction. Lloydminster Plot 6E was singled out for the degradation study since the extracted oil from this plot had the highest asphaltene content according to last year's reckoning. After air drying in the fume hood for a couple of days, a total sample of 1001 g, containing ca. 200 g from each of the 5 replicates within the plot, was prepared. The composite sample was mixed and then extracted in approximately 150 g portions in two Soxhlet (Dean-Stark adapted) apparati. This treatment was necessary since there was no Soxhlet equipment available which was large enough to handle the entire sample at one time. The extraction with toluene was continued for ca. 4 hours, by which time the extracting solvent appeared colourless. The extracted soil was eventually all recombined and dried in a vacuum oven. Likewise, the toluene extracts were mixed and filtered, and the solvent removed by rotary evaporation. Recoveries were as follows: oil, 53.5 g; soil, 909.1 g; and water, 25.6 g.

4.2.2.3.2 Fractionation. The oil was redissolved in toluene (54 mL), then hexane (1 L) was added. After settling for several hours, the asphaltenes were collected by filtration through a glass filtering funnel. They were rinsed with hexane until the solvent ran clear and colourless. The asphaltenes were removed and dried in a vacuum oven. The maltenes were reclaimed by rotary evaporation of the hexane.

Recoveries were as follows: asphaltenes, 9.76 g; and maltenes, 42.06 g.

The maltene fraction was then chromatographed on silica gel (421 g). The column was first eluted with hexane (to remove the oil fraction), next with methylene chloride (to remove a less polar resin fraction, referred to as resin-1), and finally with freshly distilled THF (to remove a more polar resin fraction, referred to as resin-2). Solvents were taken off by rotary evaporation.

The proportions of components in the extracted oil can be broken down accordingly:

total extracted oil	53.50 g
asphaltenes	9.76 g (18.2%)
oils	25.30 g (28.6%)
resin-1	14.47 g (27.1%)
resin-2	11.09 g (20.7%)
loss	2.88 g (5.4%)

All 4 oil fractions were submitted for CHN analysis. Since time was short and the results were slow in coming, it was decided to proceed with the chemical degradation. Asphaltenes normally have the highest heteroatom content, so they were selected for further reaction.

4.2.2.3.3 Depolymerization. Depolymerization is a degradative technique developed by K.A. Gould (1978) to aid in the structural analysis of coal. Depolymerization using phenol and an acid catalyst has the advantage of degrading complex organic structures by removing aliphatic sidechains and linkages from and between aromatic nuclei. The aromatic units, no longer incorporated into high molecular weight structures, became easier to isolate and therefore identify. In a sense, this is a chemical mimicry of biodegradation which occurs more readily on aliphatic hydrocarbons; the aromatic hydrocarbons are less easily metabolized so will persist longer in the soil. Both chemical and biological degradation processes act preferentially upon the aliphatic moieties; however, the aromatic moieties released will probably be of different forms. The depolymerization produces unsubstituted aromatics, while the biodegradation likely generates quinones or hydroxy-substituted

aromatics. Short of carrying out a microbial degradation under laboratory conditions and observing actual degradation products over an extended period of time, this chemical route offers relatively quick results.

Prior to setting up the reaction, some of the required reagents were purified. Phenol was distilled and the acid catalyst, para-toluene sulphonic acid (PTSA) was recrystallized from chloroform. Phenol (10.35 g), PTSA (1.50 g), and asphaltenes (5.00 g) were measured into a 500 mL round-bottom flask fitted with a dry condenser, heating mantle, magnetic stirrer and stirring bar. The flask was shielded from light with aluminum foil. The phenol mixture was then refluxed for 24 hours, then allowed to cool. Distilled water (~200 mL) was added, and stirring maintained for at least several hours. Chloroform was added and the entire contents of the flask transferred to a separatory funnel. After shaking and separation, the organic phase was drained in order to remove the aqueous phase. The chloroform extract was shaken again with water, and the two aqueous extracts combined. This aqueous extract was fairly acidic (pH ~2.5), so would contain any basic components that had been released during the reaction. To recover the basic material, this solution was made basic with KOH (to pH ~12) and then extracted with chloroform (2 x 200 mL). The combined chloroform extracts were dried over anhydrous Na_2SO_4, filtered, and the solvent evaporated to yield the "basic" products.

Returning to the original chloroform extract comprised of the bulk of the products, this solution was dried over anhydrous Na_2SO_4 which was then removed by filtration. The chloroform along with some residual phenol was taken off by rotary evaporation. The next step was to effect the separation of toluene-soluble and toluene-insoluble products, since the soluble portion consists of those products more completely degraded than the insoluble one. Toluene (~500 mL) was added to the flask containing the depolymerization products, and the mixture allowed to stir overnight. The two fractions were isolated by filtration. In summation, 4.66 g toluene-solubles and 3.05 g toluene-insolubles were recovered, implying a weight gain of 2.71 g due to phenol incorporation.

In order to simplify the eventual product analysis, the toluene-solubles were fractionated. Toluene (~300 mL) was reintroduced to the toluene-solubles, and the resulting solution extracted twice with 10% aqueous KOH. Although this step produced an emulsion, the separation of the two phases could be achieved by waiting a couple of hours. The organic phase was dried over anhydrous Na_2SO_4, filtered, and the toluene evaporated to yield a "neutral" fraction. The basic aqueous phase was acidified to pH $\simeq$3 using aqueous HCl, then extracted with toluene (2 x 250 mL). This toluene extract was dried, filtered, and the solvent taken off to yield a "phenolic/acidic" fraction. The pH of the remaining aqueous acidic phase was brought up to ~6, then an extraction with chloroform was carried out. The chloroform extract was dried, filtered, and the solvent removed to yield a "polar" fraction. The toluene-soluble products were broken down into 4 fractions of the following amounts and proportions: neutrals, 3.04 g (65.2%); phenols/acids, 0.46 g (9.9%); polars, 0.37 g (7.9%); and bases, 0.003 g (0.1%). A loss of 17% was incurred by this procedure.

GC analyses were conducted on the 4 product fractions. It was decided to attempt to clean up the samples prior to GC/MS analysis, so small portions of the neutral (0.8 g) and the acidic/phenolic (0.3 g) fractions were chromatographed on alumina (neutral activity). The polar fraction was disregarded since the GC analysis showed it to be identical to the acidic/phenolic fraction. Two columns were prepared in hexane, each containing 20 g activated alumina. Each sample was dissolved in methylene chloride and then adsorbed onto a small amount (~3 g) of alumina. The solvent was blown off under a stream of N_2. Once dry, the sample could be transferred with relative ease to the head of the column. Both columns were eluted first with hexane, then with benzene, and finally, with methylene chloride until 100, 150, and 150 mL were collected,respectively. All six samples were re-analyzed by GC.

4.2.2.4 Procedure for plant uptake analysis

4.2.2.4.1 Recovery test using new procedure. Barley spikes collected last year from plot 4W at the Lloydminster site were ground to a fine powder using a Wiley mill (with 1 mm mesh size). Four 5 g samples were each spiked with seven deuterated standards representing four classes of organic compounds: acidic, basic, aliphatic, and aromatic. Equal amounts (500 µL) of naphthalene d_8, anthracene d_{10}, chrysene d_{12}, dibenzothiophene d_8, phenol d_6, quinoline d_7, and hexadecane d_{34}, all of approximately 1 mg/mL concentration, were measured into the 4 samples by syringe. Some methylene chloride was then added to each sample to increase its mobility and allow the tracers to be more evenly distributed by stirring. The sample bottles (actually 50 mL centrifuge tubes) were loosely capped and placed in the fume hood overnight; by morning, the solvent had evaporated.

Three of the samples were handled in the exact same manner to test not only the recoverability but also the variability in the recovery of the standards, while the fourth was treated in a slightly different way for the sake of comparison. A blank sample was run at the same time. The three samples were extracted in acetonitrile (35 mL) by sonification for 2 minutes using a Brinkmann Polytron Homogenizer. The probe generator was immersed directly into each centrifuge tube which was cooled in an ice bath during the process. Use of small-mouthed centrifuge tubes as opposed to beakers for the sonification step not only saves a transference step (since centrifugation follows), but also minimizes loss from splashing or vaporizing. Samples were centrifuged for 10 minutes, the supernatant liquid decanted, and fresh acetonitrile added. The plant material was thoroughly mixed and the samples recentrifuged. Since the first rinse resulted in a strongly coloured (yellow) extract, it was decided to rinse again. The second rinse produced a nearly colourless extract so this step was not repeated.

Concurrently, the fourth plant sample was extracted with methylene chloride in a conventional Soxhlet appratus. The extraction was terminated after 4 hours, and the methylene chloride extract filtered through a glass filtering funnel to remove plant particles.

The 4 plant extracts (3 in acetonitrile, 1 in methylene chloride) were then treated in an identical manner. The extract was poured into a flask containing 500 mL distilled water plus 30 g dissolved NaCl. The solution was made basic by the addition of 6N NaOH (to a pH ~12). The sample was transferred to a separatory funnel and methylene chloride was added (only in the case of the 3 acetonitrile extracts). After agitation, the organic phase was drained off and the aqueous base rinsed once more with fresh methylene chloride. This step should partition acidic components into the aqueous base, and neutral plus basic components into the organic solvent. The basic aqueous phase was acidified with 6N H_2SO_4 to pH ~3, and extracted with two portions of methylene chloride. This should regenerate any dissolved acids and effect their recovery in the organic phase. Meanwhile, the neutral/basic fraction was extracted twice with 6N H_2SO_4. Neutral components alone should remain in the methylene chloride layer, while basic components should dissolve in the aqueous acid. Basic components were retrieved by adjusting the pH of the aqueous phase to ~12 with 6N NaOH, and extracting with two portions of methylene chloride. Therefore, three product fractions resulted from each plant extract: an acidic, a basic, and a neutral. Each of the 12 fractions was dried over anhydrous Na_2SO_4, filtered, and the solvent reduced to approximately 2 mL by rotary evaporation.

Four 20 g alumina columns were prepared in pentane. Each of the neutral fractions was adsorbed onto a small amount of alumina, and the solvent allowed to evaporate. The sample and alumina were then introduced to the top of each column and the elution process begun. Pentane (75 mL), followed by hexane (50 mL) were eluted and then combined to yield the aliphatic fraction. Next, toluene (150 mL) and finally, methylene chloride (150 mL) were collected to yield an aromatic and polar fraction, respectively. All solvents were removed by rotary evaporation. Analysis by GC was carried out on all product fractions and the recovery of the deuterated standards measured.

4.2.2.4.2 <u>New procedure applied to 1987 barley</u>. It has been assumed that the higher the concentration of oil in the soil, the higher the probability of uptake by the plant. Good growth was always associated

with soil of low oil content, so plots exhibiting such growth were unsuitable for analysis. On the other hand, poor growth was always observed on plots having high oil content; however, barley grown on these plots either produced very little or no grain. Plot 4W was finally chosen for the uptake study since the oil content was relatively large (5.96%), yet the barley supplied barely enough grain for the experiment.

A total of 4 samples were prepared, grain and straw samples each from Plot 4W and from a control site well removed from the land-treatment site. Each 10 g sample was a combination of 2 g from each of the 5 sampling points. Samples were weighed before (10.0 g) and after (~9.7 g) grinding; a slight loss was incurred during the pulverization process.

Samples were twice the size of those run in the recoverability tests, so were each divided into two equal portions in two centrifuge tubes. The larger sample sizes filled the tubes too much and would permit extraction with too little solvent. Acetonitrile (35 mL) was added to each tube and the samples homogenized in the usual manner. All 8 tubes were then centrifuged; the centrifugates derived from identical samples were decanted and combined. Each plant sample was recentrifuged twice more using fresh solvent. The resulting 4 extracts (plus rinsings) were filtered, and the volume (close to 200 mL) reduced to ~50 mL on the rotary evaporator. The presence of too much acetonitrile interferes with the subsequent partitioning since acetonitrile has high solubility not only in most common organic solvents, but also in water.

Each extract was poured into a flask containing aqueous NaCl (30 g in 500 mL distilled water) and, from this point onwards, the series of extractions and fractionations was almost indistinguishable from that described in Section 4.2.2.4.1. The one exception was the exclusion of hexane as an eluting solvent during the column chromatography of the neutral components. Pentane alone was used (100 mL being collected) since it was discovered that hexane tended to remove low molecular weight aromatics as well as aliphatics. Each plant extract eventually yielded acidic, basic, aliphatic, aromatic, and polar fractions, and all 20 fractions were analyzed by capillary GC.

4.2.3 Sample Analysis

4.2.3.1 Oil content analysis. Carbon contents of the soils were measured using a LECO CR12 Carbon Determinator. Both oil-containing and oil-free (extracted with toluene) soils were analyzed. The difference in carbon content can be related to the oil content and an oil:solids ratio can be calculated.

4.2.3.2 GC analysis. Samples from the degradation and plant uptake studies were analyzed by capillary gas chromatography with flame ionization detection (GC/FID). GC conditions were as follows:

injector temperature	250°C
detector temperature	250°C
initial temperature	50°C
hold time	2 min
program rate	5°C/min
final temperature	250°C
hold time	10 min
run time	52 min

The gas chromatograph (Varian 3400) contained a 15 m SE 54 narrow bore capillary column. Sample volumes were adjusted depending on organic content; volumes tended to be less than 100 µL. Methylene chloride was used as the solvent. Injections were 0.1 µL.

4.2.3.3 Recoveries of the deuterated standards. Deuterated standards were added to the four 1986 samples of barley spikes. Their recoverability is an indication of the success of the extraction procedure. A known concentration of each standard was injected and the GC response (peak area) to each was noted. Peak areas were then obtained for all the standards recovered in the extracts. A comparison of the two, coupled with a knowledge of the sample volume, can yield the amount of recovered standard. Average recoveries for the 4 test runs along with the relative standard deviations are discussed in Section 4.3.3.1

4.2.3.4 GC/MS analysis. Selected samples from the asphaltene degradation and the plant uptake were studied by GC/MS. Analyses were carried out on a Finnigan 4500 GC/EI Mass Spectrometer System. The gas chromatograph was fitted with a 30 m SE 54 wide bore capillary column. The GC conditions differed slightly:

injector temperature	275°C
initial temperature	50°C
hold time	1 min
program rate to 100°C	20°C/min
program rate above 100°C	5°C/min
final temperature	300°C
hold time	10 min
run time	53.5 min

Sample volumes varied from sample to sample. In the case of the plant extracts, the aromatic, polar and basic frations were diluted with methylene chloride to between 20 and 50 µL, and the acidic fractions to between 200 and 300 µL. Injections were 0.5 µL. In the case of the asphaltene degradation products, sample volumes ranged from 50 µL (for the basic fraction), to 7 mL (for the neutral aromatic fraction). Methylene chloride was again used as the solvent. Injections were 0.2 µL.

4.3 RESULTS

4.3.1 Oil Contents and Degradation in the Soil at Lloydminster

Oil to solids ratios were determined for 80 soils samples collected from all 16 Lloydminster subplots. The results for the five replicates from each subplot were aveaged, yielding one characteristic oil content value for each subplot. These 1987 data are combined with those determined in September 1986 and are shown in Table 2. A positive value in the percent degradation column suggests an apparent gain of oil over the last year, while a negative value signifies an apparent decrease in oil. It is obvious from the comparisons in Table 2 that each and every one of the 16 subplots revealed a decrease in oil.

Table 2. Degradation of oil at the Lloydminster site since September 1986.

Plot	Oil:Solids Ratio ± SD. (Sept. 4, 1986)	C.V. %	Oil:Solids Ratio ± SD. (Oct. 2, 1987)	C.V. %	% Degradation
1W	2.61 ± 0.47	18	2.13 ± 0.50	23	-18.4
2W	5.26 ± 1.04	20	4.91 ± 1.50	30	- 6.6
3W	4.85 ± 0.71	15	4.25 ± 0.21	5	-12.4
4W	4.01 ± 1.18	29	2.88 ± 0.61	21	-28.2
5W	5.22 ± 1.36	26	4.58 ± 1.08	24	-12.3
6W	5.46 ± 1.47	27	4.39 ± 0.57	13	-19.6
7W	5.16 ± 0.71	14	4.53 ± 0.74	16	-12.2
8W	3.38 ± 0.99	29	3.05 ± 1.05	34	- 9.8
1E	3.59 ± 0.61	17	2.72 ± 0.58	21	-24.2
2E	5.95 ± 0.51	9	4.67 ± 0.62	13	-21.5
3E	5.97 ± 0.61	10	5.35 ± 0.38	7	-10.4
4E	7.05 ± 0.87	12	5.96 ± 0.63	11	-15.5
5E	7.88 ± 1.07	14	6.71 ± 0.31	5	-14.8
6E	5.12 ± 0.99	19	4.97 ± 0.74	15	- 2.9
7E	6.83 ± 0.83	12	6.15 ± 0.57	9	-10.0
8E	8.58 ± 1.30	15	6.97 ± 1.16	17	-18.8

In the preceeding year, when the 1986 data were matched against those of 1985, more increases than decreases were in evidence. Since no oil had been added to the site since 1985, an increase in oil was clearly impossible; however, local increases in oil may be feasible considering that cultivation will alter the already inhomogeneous distribution of oil in the soil. A change in sample handling between those two years would also contribute to the wide fluctuations in the extent of degradation. From 1986 onwards, soils were sieved to eliminate stones and plant material and to break down oil aggregates, while prior to that time no such rigorous routine was followed. Consequently, the fluctuations in the extent of degradation between 1986 and 1987, during which years the soil samples underwent consistent treatment, were much smaller. Decreases were observed in all subplots, and although inhomogeneity of the oil may still be partly responsible for differences in oil content, the sheer uniformity of the results would seem to confirm the continuing disappearance of the oil. Variability, as indicated by the average coefficient of variations, decreased slightly from 1986 to 1987 from 17.9% to 16.5%. Variability was less on the east plots than on the west plots where oil contents were generally lower.

This year control samples were collected well outside of the perimeter of the site, rather than on the border as was done last year. The 1986 control soils were found to contain measureable quantities of oil, whereas this year, all 5 control samples were proven oil-free.

4.3.2 Asphaltene Content

Asphaltene contents were determined for each of the 16 subplots of the Lloydminster site. These values, as a percentage of the extracted oil, are listed in Table 3, and are compared to those measured for 1986. The change in asphaltenes over the past year is also included in the table, with positive values indicating an increase, and negative values a decrease.

The proportion of asphaltenes in the soil was also calculated. These data are shown in Table 4, where they are matched against last year's results, and the difference between the two years is reported.

Consideration of both asphaltene contents is important since one does not necessarily imply the other. A low asphaltene content in the oil may be linked to a high asphaltene content in the soil if the oil content is low. The same applies to a high asphaltene content in the oil. The determining factor appears to be the amount of oil in the soil; the higher the oil content, the higher the asphaltene concentration in the soil. This is indeed substantiated if the 16 oil:solid ratios are ordered sequentially from lowest to highest; the asphaltene: solid ratios follow an almost identical sequence (only the values for plots 2E and 3W are slightly out of order). The same trend does not apply for the proportion of asphaltenes in the extracted oil.

A trend towards increasing asphaltenes in the oil is clear in Table 3. In 12 out of the 16 subplots, an increase is noted. If the respective increases/decreases are viewed in the light of the extent of degradation of the oil, the following observations emerge:

1. a small reduction in the oil content of the soil resulted in either a small increase or decrease in the proportion of asphaltenes;
2. a medium reduction in the oil content of the soil resulted in either a small or medium increase in the proportion of asphaltenes; and
3. a large reduction in the oil content of the soil resulted in either a medium or large decrease in asphaltenes.

where increases or decreases of 0 to 10%, 10 to 20%, and above 20% are considered to be small, medium, and large, respectively. In other words, only asphaltenes in plots exhibiting maximum biodegradation were apparently degraded.

Although the proportion of asphaltenes in the oil appears to be on the rise, the actual concentration of asphaltenes in the soil has gone down in all cases.

Table 3. A comparison of asphaltene contents of the oil extracted from each Lloydminster subplot in 1986 and 1987.

Plot	% Asphalenes (1986)	% Asphaltenes (1987)	% Increase (+)/ Decrease (-)
1W	15.90	18.33	15.3
2W	19.31	19.51	1.0
3W	19.29	22.20	15.1
4W	15.38	20.89	35.8
5W	18.46	19.61	6.2
6W	18.45	19.76	7.1
7W	20.62	19.48	- 5.2
8W	18.53	20.69	11.7
1E	21.54	15.93	-26.0
2E	19.58	17.23	-12.0
3E	18.27	18.79	2.8
4E	17.64	20.51	16.3
5E	17.42	18.93	8.7
6E	21.88	19.96	- 8.8
7E	20.34	20.47	0.6
8E	19.81	19.99	0.9

Table 4. A comparison of asphaltene contents of the soil from each Lloydminster subplot in 1986 and 1987.

Plot	% Asphaltenes (1986)	% Asphaltenes (1987)	% Increase (+)/ Decrease (-)
1W	0.41	0.39	- 4.9
2W	1.02	0.96	- 5.9
3W	0.94	0.94	0.0
4W	0.62	0.60	- 3.2
5W	0.96	0.90	- 6.3
6W	1.01	0.87	-13.2
7W	1.06	0.88	-17.0
8W	0.63	0.63	0.0
1E	0.77	0.43	-44.2
2E	1.17	0.80	-31.6
3E	1.09	1.01	- 7.3
4E	1.24	1.22	- 1.6
5E	1.37	1.27	- 7.3
6E	1.12	0.99	-11.6
7E	1.39	1.26	- 9.4
8E	1.70	1.39	-18.2

4.3.3. Plant Uptake Analysis

4.3.3.1 Recovery of standards. The four sets of product fractions derived from the barley spikes harvested in 1986 were analyzed by capillary GC/FID. No GC/MS analyses were conducted since the purpose of this part of the study was merely to quantify the recovery of the various tracers, a task which can be accomplished entirely using a gas chromatograph.

Three samples were extracted using a Brinkmann Polytron Homogenizer (referred to as PE-1, PE-2, and PE-3) and a fourth was extracted using methylene chloride in a conventional Soxhlet apparatus (referred to as SE-1). The samples had been spiked with seven deuterated standards, all of which showed up in the fraction in which they were expected. Naphthalene, anthracene, dibenzothiophene, and chrysene were all recovered in the aromatic fraction, hexadecane (and sometimes naphthalene) in the aliphatic fraction, phenol in the acidic fraction, and quinoline in the basic fraction. Naphthalene probably eluted with the aliphatics when hexane was run through the alumina column, so in the subsequent fractionations (i.e., of extracts from the recently harvested barley), hexane was avoided.

Average recoveries plus percent relative standard deviations are listed in Table 5. The Soxhlet-extracted results represent only a single set of data so the variability is not known.

In the PE series, phenol was not the only standard revealed in the acidic fraction. Small amounts (7% on average) of the other standards, excepting quinoline, were appearing there also. The first extraction procedure in the fractionation process attempts to separate neutral and basic species from acidic species. This is accomplished by shaking the plant extract, in acetonitrile, with methylene chloride and aqueous base. The presence of the acetonitrile will likely result in inefficient partitioning of the standards into the organic phase. Acetonitrile has high solubility in both water and methylene chloride, so the affinity of the neutral standards for the aqueous phase will necessarily be enhanced. Once in the aqueous phase with the supposedly acidic components, they will eventually be recovered in a subsequent extraction. Concern for this slight transfer of neutral substances

into aqueous solution lead to the recommendation that the volume of the original acetonitrile extract be reduced before proceeding with the fractionation steps. This precaution was indeed taken when the 1987-harvested barley was processed.

There was some trouble associated with the recovery of the more volatile standards. The recoveries of naphthalene, for instance, covered a broad range, a problem which was probably aggravated by the long lapse of time between the completion of the separation procedure and the GC analysis. The gas chromatograph was inoperational for several weeks, and although samples were tightly sealed and stored under refrigeration in the meantime, losses may still have occurred. The same applies to phenol, and in both cases the lowest recovery value

Table 5. Average recoveries of deuterated standards from the extraction and fractionation of 1986 barley.

Standard	PE Series % Recovery	SE % Recovery
naphthalene d_8	55.3 ± 30.0	72.1
dibenzothiophene d_8	90.0 ± 7.4	32.1
anthracene d_{10}	83.6 ± 10.4	29.8
chrysene d_{12}	125.1 ± 9.9	11.0
hexadecane d_{34}	98.7 ± 0.7	57.7
phenol d_6	81.0 ± 9.4	2.9
quinoline d_7	97.9 ± 0.5	68.4

was discarded (their standard deviation calculations were, therefore, based on 2 rather than 3 results).

Anomolous behaviour was seen in the recovery of chrysene which showed a return in excess of 100%. This phenomenon can only be explained by the existence of some component, either extracted from the barley or present as an impurity, which co-eluted with the chrysene, thus magnifying its peak area in the GC trace. The blank aromatic run

did exhibit a peak with the same retention time as that of chrysene, so the peak inflation may indeed have been caused by some extraneous substance.

Regardless of these unavoidable complications, the recoveries from the Polytron extraction technique were generally good and obviously superior to those from the Soxhlet extraction technique. Methylene chloride did not appear to be an adequate solvent for extracting a wide variety of chemical compounds from plant material. Acetonitrile accomplished the task not only more effectively but also more quickly.

4.3.3.2 GC analysis of 1987 barley extracts. Grain and straw extracts from Plot 4W and a control site were each separated into five fractions. The 20 resulting fractions were analyzed by GC/FID. The peaks occurring in the GC traces of the two sets of straw samples (from Plot 4W and the control) were cross-referenced; the same was done for the two sets of grain samples. Almost all the peaks appearing in the Plot 4W straw and grain aliphatic fractions could be accounted for in the same fractions of the control straw and grain. All the major components in the Plot 4W aromatic fractions could be matched with corresponding components in the control aromatic fractions. In the polar fractions, some of the predominant constitutents in the Plot 4W samples appeared not to be in evidence in the control samples, while in the acidic fractions, nearly all of the major components in the Plot 4W samples had counterparts in the control samples. Basic fractions showed only few differences. Confirmation of similarities or dissimilarities must await the GC/MS analysis which will provide identities for the components of the extracts.

4.3.3.3 GC/MS analysis of the 1987 barley extracts. Not all of the 20 plant samples underwent GC/MS examination. The aromatic, polar, acidic and basic fractions derived from the barley grain and straw grown on Plot 4W (8 samples in all) were analyzed in depth. The aliphatic fractions were omitted from this study because they accounted for such a minute proportion of the total extract. Gas chromatography detected only barely discernible peaks in these fractions, even though the

volumes of the the two samples were reduced to 10 µL. In any event, the aliphatic components are of the least concern.

Time was also short, and would not permit the analysis of too many samples. Regrettably, a corresponding analysis of all of the control samples could not be carried out. Since the extracts appeared to be predominantly acidic in nature, it was decided to investigate just the two acidic fractions from the control grain and straw. In total, 10 samples were scrutinized.

It must be made clear that not every mass spectrum could be interpreted. The structures listed are those for which an excellent match could be made to a known spectrum. The only exceptions to this practice arose when considering Plot 4W straw, three components of which (the substituted indolenine, benzoquinoline and thiophene) may not exist in the structures as reported. Their agreement with the corresponding literature spectra was not exceptional, and the true structures may indeed be different; however, the fragmentation patterns observed were typical of such types of compounds. It was felt necessary to reveal their presence even in the face of doubtful identification, because they seemed to represent substances more characteristic of oil than plants.

The major components of all four plant extracts were long chain fatty acids, ranging in length from 8 to 18 carbon atoms. Of these, three acids predominated: palmitic (P), linoleic (L) and stearic (S) acids. The amounts of these three particular acids (which will be subsequently referred to as the PLS total) varied dramatically between samples obtained from oil-free soil and from oil-treated soil. The PLS total in the Plot 4W straw was 68 ppm, about 2½ times the amount (28.5 ppm) in the control straw. Surprizingly, the PLS total in the Plot 4W grain was 309 ppm, almost 14 times the concentration in the control grain (22.4 ppm). The grain procured from barley raised on oily soil is obviously concentrating the naturally-occurring acids for unknown reasons.

The relative proportions of these three acids were similar in three out of the four samples even though the total amounts were widely different. The linoleic acid was always present in the highest amount, followed by the palmitic acid, with stearic acid having the lowest

amount. The approximate relative proportions of palmitic acid to linoleic acid to stearic acid were 6:8:1. In contrast, the Plot 4W straw sample was distinctive from the other three by the absence of any linoleic acid. Apparently something was physiologically wrong with the crops from the sludge-treated soil such that some fatty acids were overproduced while others were not produced at all. The grain seems to be more susceptible to overproduction, and the straw to underproduction.

Results for the four original extracts were condensed and are presented in simplified form in four separate sections. Quantities were estimated using comparisons between the areas of reference materials of known concentration and the areas of the authentic components as provided by the GC/FID analyses.

4.3.3.3.1 Sample: Plot 4W Straw

General class of compounds identified by GC/MS:

1. aliphatic acids
2. ketones and aldehydes
3. aromatic acids
4. miscellaneous compounds

	Specific Compounds Identified	Approximate ppm
	<u>Aliphatic Acids</u>	
1.	$C_7H_{15}COOH$	0.4
2.	$C_8H_{17}COOH$	0.2
3.	$C_9H_{19}COOH$	0.3
4.	$C_{10}H_{21}COOH$	0.4
5.	$C_{11}H_{23}COOH$	1
6.	$C_{13}H_{27}COOH$	7
7.	$C_{14}H_{29}COOH$	1
8.	$C_{15}H_{31}COOH$ (palmitic acid)	56
9.	$C_{16}H_{33}COOH$	2
10.	$C_{17}H_{35}COOH$ (stearic acid)	12

	Specific Compounds Identified	Approximate ppm
	Ketones and Aldehydes	
1.	$CH_3-\overset{O}{\overset{\|\|}{C}}-C_{11}H_{23}$	0.3
2.	$CH_3-\overset{O}{\overset{\|\|}{C}}-C_{15}H_{27}$	7
3.	$CH_3-\overset{O}{\overset{\|\|}{C}}-C_{15}H_{31}$	2
4.	$Ph-CH=CH-\overset{O}{\overset{\|\|}{C}}-CH_3$	6
5	$CH_3-(CH_2)_4-CH=CH-CH=CH-CHO$	0.2
	Miscellaneous Compounds	
1.	1,2-dithiane	0.03
2.	benzothiazole	0.02
3.	3-methyl-3-ethylindolenine	0.1
4.	2-nbutylthiophene	0.03
5.	CH_3-benzoquinoline	0.3
6.	phthalic anhydride	0.05
7.	S_8	?

4.3.3.3.2 Sample: Plot 4W Grain

General class of compounds identified by GC/MS:

1. aliphatic acids
2. ketones and aldehydes
3. aromatic acids
4. miscellaneous compounds

Specific Compounds Identified	Approximate ppm
Aliphatic Acids	
1. $C_7H_{15}COOH$	0.04
2. $C_{10}H_{21}COOH$	0.08
3. $C_{13}H_{27}COOH$	0.9
4. $C_{15}H_{31}COOH$ (palmitic acid)	132
5. $C_{17}H_{31}COOH$ (linoleic acid)	161
6. $C_{17}H_{35}COOH$ (stearic acid)	16
Ketones and Aldehydes	
1. $CH_3-\overset{O}{\overset{\|}{C}}-C_{15}H_{27}$	0.2
2. $CH_3-\overset{O}{\overset{\|}{C}}-C_{15}H_{31}$	0.1
4. $Ph-CH=CH-\overset{O}{\overset{\|}{C}}-CH_3$	1
5 $CH_3-(CH_2)_4-CH=CH-CH=CH-CHO$	1

Specific Compounds Identified	Approximate ppm
Miscellaneous Compounds	
1. naphthalene	0.003
2. 1,2-dithiane	0.1
3. terpene alcolhols	0.02
4. alkenes	80

4.3.3.3.3 Sample: Control Straw

General class of compounds identified by GC/MS:

1. aliphatic acids
2. aromatic acids
3. miscellaneous compounds

Specific Compounds identified	Approximate ppm
Aliphatic Acids	
1. $C_9H_{19}COOH$	0.2
2. $C_{13}H_{27}COOH$	2
3. $C_{14}H_{29}COOH$	0.3
4. $C_{15}H_{31}COOH$ (palmitic acid)	11
5. $C_{16}H_{33}COOH$ (linoleic acid)	14.5
6. $C_{17}H_{35}COOH$ (stearic acid)	3
Aromatic Aldehydes	
1. 4-hydroxybenzaldehyde	0.2
2. vanillin (4-hydroxy-3-methoxybenzaldehyde)	1

	Specific Compounds Identified	Approximate ppm
	Miscellaneous Compounds	
1.	2,6-dimethoxy-1,4-benzoquinone	0.8
2	$C_{16}H_{30}O$	7

4.3.3.3.4 Sample: Control Grain

General class of compounds identified by GC/MS:

1. aliphatic acids
3. aromatic acids

	Specific Compounds Identified	Approximate ppm
	Aliphatic Acids	
1.	$C_{17}H_{15}COOH$	0.05
2.	$C_{10}H_{21}COOH$	0.01
3.	$C_{13}H_{27}COOH$	0.1
4.	$C_{15}H_{31}COOH$ (palmitic acid)	7
5.	$C_{17}H_{31}COOH$ (linoleic acid)	14
6.	$C_{17}H_{35}COOH$ (stearic acid)	1.4
	Aromatic Acids	
1.	benzoic acid	0.03

4.3.4 Chemical Degradation

4.3.4.1 CHN analyses. Oil extracted from Plot 6E was fractionated into asphaltenes, oils and two resins (a less and a more polar variety). All four fractions were submitted for analysis to the Chemistry Department of the University of Calgary. Although carbon, hydrogen and nitrogen contents were requested, for some unknown reason only carbon and hydrogen results were reported. Since the degradation had already proceeded on the asphaltenes, it was inconsequential at this stage to pursue the missing nitrogen data. In any even, the respective C and H contents are presented in Table 6. Since C and H do not account for 100% of the composition, the remainder was presumed to be comprised of heteroatoms (nitrogen, oxygen and sulphur).

Table 6. Carbon, hydrogen and heteroatom contents of components of the oil extracted from Plot 6E.

Sample	% C	% H	% N,O,S	H/C ratio
Oils	84.60	11.32	4.08	1.61
Resin-1	80.11	9.74	10.15	1.46
Resin-2	77.76	10.10	12.14	1.56
Asphaltenes	81.41	8.42	10.17	1.24

The three liquid fractions were analyzed for sulphur using a Princeton Gamma Chemical Analyzer (model 100); this instrument is incapable of handling solid samples, i.e. asphaltenes. Analyses were performed in triplicate, and the following average values were determined: oils, 1.93%; resin-1, 10.36%; and resin-2, 8.93%.

It had originally been planned to carry out the depolymerization reaction on the fraction of the extracted oil having the highest heteroatom content. At first glance, it appears that the wrong choice

was made since the resin-2 fraction, rather than the asphaltenes, shows a greater proportion of heteroatoms. However, some evidence to the contrary soon came to light. While heating up the two sticky resin samples to facilitate sample removal for the sulphur analysis, it became obvious from the distinctive odour that resin-2 still contained THF (the solvent used to elute this fraction from silica gel). Therefore, the combined N, O, S content has evidently been inflated by the presence of this oxygen-bearing solvent. The extent of inflation cannot be estimated without knowing the amount of residual solvent, so any comparison of heteroatom contents is essentially ineffectual.

The sulphur content of resin-1 was determined to be slightly higher than the total N, O, S content according to the CH analysis. This is not too unreasonable if one considers the nature of the sample as well as the technique involved. All oil samples are complex mixtures, and it is difficult to guarantee a homogeneous sample when it exhibits the extreme viscosity of resin-1. It is entirely possible that the small sample removed for the CH analysis may not have been representative of the whole, especially since only one analysis was performed. Several analyses would have allowed the calculation of average carbon and hydrogen contents which would have been more illustrative of the sample's composition.

A chemical analysis of the asphaltenes as opposed to the other fractions was fully justified, no matter what the heteroatom content. The H/C ratio revealed that, from a structural point of view, asphaltenes bear little resemblance to the other 3 fractions. They display far more aromatic character, and for this reason should be more slowly metabolized by soil microorganisms. Their potential to release harmful organics at some point in the future should be assessed, and a structural study is one way of accomplishing this.

4.3.4.2. GC/FID analysis. GC spectra were recorded for the 4 product fractions from the depolymerization reaction (neutral, basic, acidic/phenolic, and polar fractions). It was decided to chromatograph the neutral and acidic/phenolic fractions prior to GC/MS analysis; in order to avoid repetition, this clean-up procedure was not applied to the polar fraction since it exhibited the same composition as the acidic/

phenolic fraction. These 2 fractions were then each separated into aliphatic, aromatic and polar fractions, and each analyzed by GC/FID.

Most of the neutral components appeared in the aromatic fraction, as expected. The aliphatic fraction revealed almost nothing, and the polar fraction only one major component.

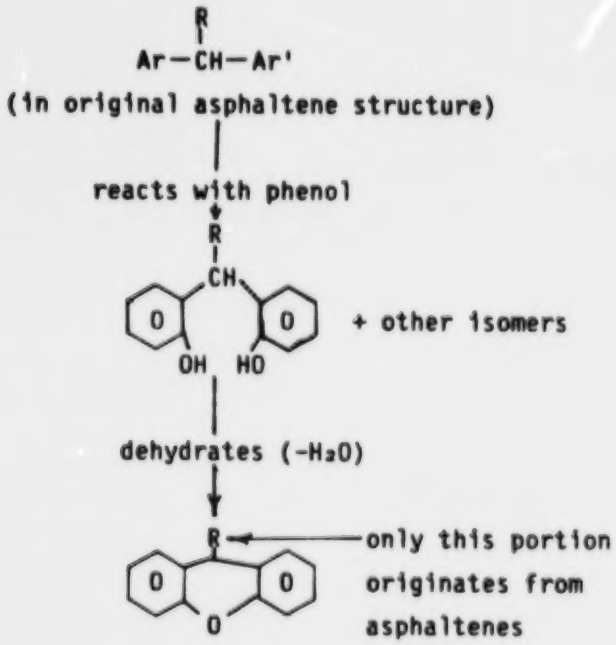
The acidic/phenolic fraction should consist of a series of aliphatic-substituted phenols (at either the ortho or para positions), as well as a series of aliphatic-bridged phenols. Both are represented as follows:

The former results when phenol essentially "removes" an aliphatic side-chain from an aromatic unit, and the latter results when two phenols react with an aliphatic bridge connecting two aromatic units. In fact, two homologous series were indeed in evidence in the GC trace of the unchromatographed sample. Unfortunately, the alumina appeared to have retained these two sets of polar by-products because they both failed to reappear in the chromatographed fractions. The aliphatic fraction showed next to nothing while the aromatic fraction displayed only a few components. Both of these observations were expected since, by the nature of the extraction procedure, components of those chemical classes should not have been present in the acidic/phenolic fraction. However, it was hoped that the substituted phenols would be eluted from the alumina column with methylene chloride. Unfortunately, this was not the case. The polar fraction yielded only one component and the two homologous series evaded detection. Luckily some of the original sample remained, and this (rather than the chromatographed products) will undergo GC/MS examination.

4.3.4.3 GC/MS analysis of the degradation products. Five samples were subjected to GC/MS analysis: a neutral aromatic and a neutral polar fraction (obtained from chromatography of the original neutral extract

on alumina), the unchromatographed acidic/phenolic fraction, a polar fraction and a basic fraction.

The neutral aromatic fraction revealed the greatest variety of aromatics, generally falling into the categories of naphthlenes, benzofurans, benzothiophenes and xanthenes. The xanthenes result from diphenolic species which dehydrate in the following sequence:



The acidic/phenolic and polar fractions were known to be almost identical from their GC traces, but in order to verify this supposition, their mass spectra were compared. Both contained, as expected, a series of alkyl-substituted phenols and a series of alkyl-connected diphenolic species. Longer series were detected in the polar fraction, accounting for the only, if somewhat minor, difference between the two. The neutral polar fraction was comprised predominantly of carbazoles, and the basic fraction of a few unimportant by-products of the reaction (there were no basic substances in evidence).

When all of the information on the asphaltene degradation products is sorted out and compiled, the following picture emerges. Asphaltenes contain:

1. Aliphatic sidechains originally attached to aromatic units. These vary from CH_3 to C_7H_{15} in length, and are either linear or non-linear. For instance, the predominant $-C_4H_9$ sidechain would be linear (i.e. $CH_2CH_2CH_2-CH_3$), but non-linear sidechains were also detected (i.e. $-CH(CH_3)-CH_2CH_3$).

   Some cycloalkyl sidechains were also discovered, e.g. cyclopentyl and cyclohexyl. These aliphatic appendages to aromatic units account for about 50 mg or 1% of the original 5 g asphaltene sample weight.

2. Aliphatic bridges originally connecting two aromatic units. These bridges consist of from one to five carbon atoms. Bridges were either linear or branched. One major series was of the following form:

$$-\overset{R}{\underset{|}{C}}H-$$

   with R in range of -H, CH_3, C_2H_5, ..., $C_{21}H_{43}$.
   These connections account for about 16 mg or 0.3% of the asphaltene weight.

3. Aliphatic bridges originally connecting three aromatic units. These are one carbon connections of the form

$$Ar-\overset{Ar''}{\underset{|}{C}}H-Ar'$$

   where one of the aromatic units is sometimes phenyl, i.e.

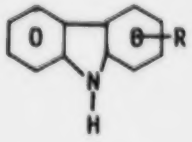
$$Ar-\overset{Ph}{\underset{|}{C}}H-Ar'$$

   These pieces of the asphaltene structure account for approximately 0.4 mg (0.008% by weight).

4. Aromatic units originally attached to the asphaltene matrix via some form of aliphatic bridge or possibly present as separate entities bearing aliphatic sidechains. In some instances, aromatic structures were identified having one or more methyl groups; this is not unusual since phenol does not readily remove methyl substituents.

The types of aromatic compounds which are easily degraded from the asphaltene structure are listed below. The identities are revealed only for those species which gave a positive match to a spectrum of the authentic substance.

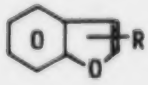
i) Carbazoles



0.42 mg (84 ppm)

R = H, $CH_3)_x$ x = 1,2,3

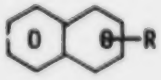
ii) Benzofurans



0.19 mg (38 ppm)

R = $CH_3)_x$ x = 2,3

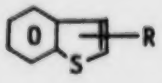
(iii) Naphthalenes



0.61 mg (122 ppm)

R = $CH_3)_x$ x = 1,2,3

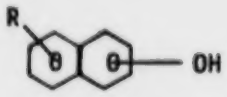
(iv) Benzothiophenes



1.82 mg (364 ppm)

$R = -CH_3)_x$ $x = 1,2,3,4$

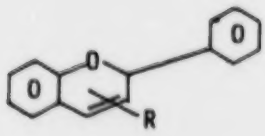
(v) Naphthols



1.24 mg (248 ppm)

$R = -H, -CH_3)_x$ $x = 1,2$

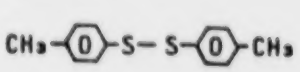
(vi) Flav-3-enes



0.28 mg (56 ppm)

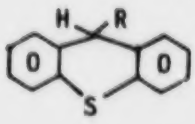
$R = -H, -CH_3 \ldots, C_{11}H_{23}$

(vii) Disulphides



0.11 mg (22 ppm)

(viii) Thianthrenes



0.23 mg (46 ppm)

$R = -CH_3, -C_2H_5$

4.4 DISCUSSION

4.4.1 Oil and Asphaltene Contents

Landtreatment as a means of disposal of oily wastes depends upon the efficiency of biodegradation by soil microorganisms. This degradation, in turn, is affected by a wide variety of factors, including the type of soil, the climatic conditons, nutrient sources, the nature and the amount of oil as well as inorganic salts, and the extent of cultivation.

The measurement of the extent of degradation of the oil on an annual basis gives some idea of its expected persistence in the soil. Last year the evidence pointed towards an apparent cessation of biodegradation at the Lloydminster site. This would imply that the remaining oil would likely linger in the soil for an extended period of time, and that sludge-treated sites could not realistically be returned to normal usage in the near future. Degradation results cannot be interpreted too strictly, though, since accurate monitoring of residual oil content is difficult; it is hampered by the inhomogeneity of the distribution of oil in the soil (a variable which changes each time the soil is cultivated) and by the possibility of fluctuating degradation rates within the site itself. Added to these obstacles which will always exist, was a change in the sample handling technique between 1985 and 1986, a fact which raised the suspicion that last year's predictions were probably somewhat premature.

As it turned out, the 1987 results forecast a different scenario than that suggested by the 1986 results. Continuing, rather than ceasing, biodegradation was observed over the entire site. Reductions over the past year varied from 3 to 28%, depending on the plot. Only 2 subplots displayed rather modest depletions; the decrease averaged a more substantial 15%. Although it must be kept in mind that the degradation measurements will be subject to the same hindrances (i.e., inhomogeneity of oil in the soil) every year, at least the sample handling was consistent so one variable has been removed. The overwhelming uniformity of the results would seem to indicate that the oil is indeed disappearing at a moderate rate and, if this rate

persists in subsequent years, the site may fully recover its former productivity within 5 to 10 years.

An attempt was made to rationalize the extent of degradation as a function of some factor typical of each subplot. For instance, one might expect a large sludge application to be linked to a slow degradation and a small one to a correspondingly rapid degradation. These expectations were unfounded, however. Those subplots having the lowest oil content tended to show among the highest extents of oil reduction but those having the highest oil contents also displayed above average decreases. Below average reductions seemed to be associated with oil contents in the range of 4.5 to 5.0%, and also with oil of high asphaltene content (based on the 1986 determinations). In any event, biodegradation is dependent on so many variable factors that any simple, straightforward correlations of this sort will be hard to pinpoint.

Asphaltenes were measured from a composite sample representing each of the 16 Lloydminster subplots. The method of determination remained unchanged for the past two years, so a comparison between 1986 and 1987 should be meaningful. The 1987 calculations showed increases in the proportion of asphaltenes in the extracted oil from 12 of the 16 subplots. Asphaltenes should be the least degradable component of the oil. As the more easily degradable oil is depleted by the soil microorganisms, a gradual accumulation of asphaltenes is anticipated and appears to be coming true. Some reductions in asphaltene content did occur but these tended to be linked with areas exhibiting high rates of oil degradation. Although the asphaltene content of the oil seems to be on the rise (with an average increase of 10%), the actual asphaltene content of the soil is dropping (with an average decrease of 11%) because the oil content is declining.

4.4.2 Plant Uptake

The results from the plant uptake study suggest that the modified extraction technique is satisfactory for recovering a wide range of chemical substances. Among the tracers used in the recoverability study, nearly all were retrieved in high yields. There were some troubles associated with the more volatile compounds but these may

probably be remedied by analyzing the samples immediately upon their isolation. The presence of impurities created other problems which, although unavoidable, were alleviated by the performance of a blank run.

The GC/FID analysis of the extracts from the 1987 - harvested barley was inconclusive. Although at first it appeared that the major differences between plants grown on oil-free and oil-treated soil were in the acidic and polar components, this assumption was later proved false. The subsequent GC/MS analysis revealed that most of the acidic species in the grain and straw from Plot 4W had counterparts in the control samples. The overproduction or non-production of some of these fatty acids in the Plot 4W samples may be indicative of a physiological problem within plants which are obviously stressed (whether by the presence of oil or salts in the soil, or for any other reason, is unknown). Aside from the obvious signs of an unhealthy plant (poor growth, little or no seed production), the relative and total amounts of palmitic, linoleic and stearic acids may be a useful fingerprinting device to establish the condition of a plant.

The straw from Plot 4W was the only sample to reveal abnormal organic substances. It is possible that these abnormalities may have originated on the outside rather than the inside of the plant material. The straw was rinsed only with distilled water prior to grinding, and any oily residue on the plant surface may not have been removed. Most of the unusual compounds were heterocyclic in nature, and would likely have moderate water solubility; therefore, it is equally probable that these substances have been taken up by the plant. The oddest discovery in the straw was elemental sulphur which is insoluble in water, and may indeed have existed only on the plant surface. Whether organic compounds are present internally or externally can only be determined by further study.

4.4.3 Chemical Degradation

Asphaltenes from Lloydminster plot 6E were chemically degraded in an effort to identify mobile components. Several product fractions were isolated according to their chemical classification and were all examined first by GC/FID, and finally by GC/MS.

Some structural elements were identified. Aliphatic side-chains and linkages were in evidence, as expected for a typical asphaltene matrix. The aromatic units which were cleaved from the asphaltene structure would be subject to all the usual removal pathways: aqueous dissolution, volatilization, photodestruction, soil adsorption and biodegradation. Each pathway is interreactive, making any hazard assessment a complex issue. Considered singly, the following picture results: naphthols have the highest water solubility, so would have a higher probability of contaminating groundwater; naphthalenes and benzothiophenes have the highest vapour pressures, so some losses to the atmosphere might occur; photolysis of organic substances is less viable on the surface of soil than in aqueous solution, so removal by this route should be minimal; adsorption of chemicals onto soil is a well-established phenomenon, with the extent of sorption increasing with increasing organic content of the soil, so retention in that phase is highly likely; biodegradation is the most probable removal pathway since most of the above-mentioned materials are known to be metabolized or co-metabolized (in the presence of other more easily-degradable organics). It is apparent that potential hazards cannot easily be predicted, especially since only a very small portion of the asphaltene structure was examined. To dwell too long on compounds comprising less than 2% of the total asphaltenes when 98% remains as yet undisclosed would be a delusion. More persistent or deleterious species may still exist, locked within the asphaltene structure. Whether or not there are toxic organics that may be released at some later date cannot be conclusively determined.

5. SOIL PRODUCTIVITY

5.1 OBJECTIVES

The objectives of the soil-plant studies were to determine the productivity of soils previously treated with oily sludges. It is the aim of the program to provide information which will permit sludge treated soils to be returned to standard agriculture uses. As observations in 1986 indicated that treatment with oily sludges could result in long term inhibition of plant growth, it was desired to determine what specific factors were limiting growth, especially oil and salt content.

5.2 MATERIALS AND METHODS

5.2.1 Soils and Plant Material

The soils and plants were sampled as described in section 3.2. Soils were submitted to the Earth Sciences Division, Alberta Environment, Lethbridge for analyses. Analyses included pH (soil paste), electrical conductivity, sodium adsorption ratio (SAR) and anions and cations in saturated extracts, total carbon, and DTPA extractable metals (Fe, Cu, Zn, Pb, Mn, Cd and Ni). Samples of straw and grain from the control site, plot 6W (sludge-treated, fair growth) and plot 8W (sludge treated, good growth) were ground in a Wiley mill (40 mesh). Five replicate samples of each were submitted to the Earth Sciences Division for digestion and analysis for heavy metals.

Soil from each of the west plot samples and the control samples were used to assess soil productivity under uniform greenhouse conditions. Subsamples of each field sample were placed in 5 inch standard pots with a layer of cheesecloth in the bottom to prevent soil from leaking out. Either 10 seeds of barley or about 50 seeds of clover were planted per pot and the pots were placed in a greenhouse. Light supplemented with 1000 w metal halide lamps to provide a 20 h day length (miniumum 20 klx). Fertilizer was applied after planting at rates equivalent to 25 kg N ha^{-1} and 5 kg P ha^{-1}. The pots were watered as needed, avoiding excessive moisture and the shoots were harvested, dried (80°C) and weighed after 5 weeks growth.

5.3 RESULTS

5.3.1 Visual Estimates of Growth

5.3.1.1 Barley growth at Lloydminster. Visual estimates of growth were made August 26, 1987 at the same time as the adjacent barley field was being harvested. All of plots 1W, 1E, 2W, 2E and the southern halves of plots 3W and 3E had been accidently cut in mid-July and thus growth could not be determined. Visual estimates of growth indicated that the amount and pattern of growth was very similar to that observed in 1986 with no obvious improvement in any treatments (Table 7). Growth in plot 8W was comparable to that in the adjacent field which served as the control standard for rehabilitation of the oil treated soils. Several western plots demonstrated variable growth (4W, 5W, 6W, 7W), probably due to uneven sludge applications. Growth was generally poor in all other plots.

5.3.1.2 Plant growth at Drayton Valley. The growth of the hay crop planted in 1986 was visually assessed October 23, 1987. Four species had been seeded in 1986 but only timothy and red rescue formed a substantial portion of the 1987 crop. Small amounts of clover were present throughout the experimental area, but no foxtail was observed. Growth generally improved as compared to 1986 and cover was nearly 100% in the treatments rated good or excellent (Table 8). Poor growth occurred in only two plots (6S, 7S) which had very poor growth in 1986. In general, growth was good to excellent when moderate amounts of sludge had been applied to the soil. Both timothy and red fescue grew well in these plots with timothy reaching heights of nearly 1 m. Weeds had not colonized the experimental area to detrimental proportions except for a few patches of thistle.

5.3.1.3 Plant growth at Grande Prairie. In 1986, growth was poor over the entire experimental area but in the second year growth had substantially improved (Table 9). Both timothy and alfalfa exhibited moderately good growth with alfalfa dominating the northern plots and timothy dominating the southern (heavy application) plots. Poor growth

Table 7. Visual estimates of plant vigor and growth of barley on the Lloydminster site (August 26, 1987) compared with 1986 results. Soil sampled October 2, 1987.

Plot	Sludge Application (year and m³)		Fert.	Cult.	Plant Growth	
					1986	1987
1W[1]	82,84,85	4.2+1.6+2.3	Low	Low	Good	NA[4]
1E	82,83,84,85	4.2+5.7+1.6+2.3	Low	Low	Good	NA[4]
2W[1]	82,84,85	8.4+1.6+2.3	High	High	V.Poor	NA[4]
2E	82,83,84,85	8.4+11.4+1.6+2.3	High	High	Poor	NA[4]
3W[1]	82,84,85	8.4+1.6+2.3	Low	High	Poor	Fair[5]
3E	82,83,84,85	8.4+11.4+1.6+2.3	Low	High	Poor	Poor[5]
4W[1]	82,84,85	4.2+1.6+2.3	High	Low	Fair	Fair-Good
$4E_{1,2}$	82,83,84,85	4.2+5.7+1.6+2.3	High	Low	Poor	Poor
5W	82,84,85	8.4+1.6+2.3	Low	Low	Poor	Poor-Fair
5E	82,83,84,85	8.4+11.4+1.6+2.3	Low	Low	Poor	V. Poor
6W[1]	82,84,85	4.2+1.6+2.3	High	High	Fair	Fair
$6E^{3}_{1,2}$	82,83,84,85	4.2+5.7+1.6+2.3	High	High	V.Poor	Poor-Fair
7W	82,84.85	4.2+1.6+2.3	Low	High	Fair	Poor-fair
$7E_{1,2}$	82,83,84,85	4.2+5.7+1.6+2.3	Low	High	Poor	Poor
8W	82,84,85	8.4+1.6+2.3	High	Low	Good	Good
8E	82,83,84,85	8.4+11.4+1.6+2.3	High	Low	Poor	V.Poor
Control		0	--	--	Good	Good

[1] Plots sampled for greenhouse study.

[2] Surface 2 cm of soil sampled for soluble salts.

[3] Plot sampled for asphaltene content

[4] Not applicable; crop assessments not possible due to cutting in July.

[5] Half of plots cut in July, estimates based on northern half of plots.

Table 8. Visual estimates of plant growth of a timothy-red fescue hay mixture on the Drayton Valley site (October 23, 1987) compared with 1986 results.

Plot	Sludge Application (year and m³)		Fert.	Cult.	Plant Growth	
					1986	1987
1N	82	12.5	High	High	Fair	Good
1S	82,83	12.5 + 6.2	High	High	Poor	Fair
2N	82	6.2	Low	Low	Good	Excellent
2S	82,83	6.2 + 3.1	Low	Low	Good	Good
3N	82	6.2	High	Low	Good	Excellent
3S	82,83	6.2 + 3.1	High	Low	Good	Good
4N	82	12.5	High	Low	Fair	Good
4S	82,83	12.5 + 6.2	High	Low	Good	Fair
5N	82	6.2	Low	High	Good	Good
5S	82,83	6.2 + 3.1	Low	High	Good	Good
6N	82	12.5	Low	Low	Poor	Fair
6S	82,83	12.5 + 6.2	Low	Low	V.Poor	Poor
7N	82	12.5	Low	High	Fair	Fair
7S	82,83	12.5 + 6.2	Low	High	V.Poor	Poor
8N	82	6.2	High	High	Good	Good
8S	82,83	6.2 + 3.1	High	High	Fair	Fair

Table 9. Visual estimates of plant growth of alfalfa and timothy on the Grande Prairie site (September 23, 1987) compared with 1986 results.

Plot	Sludge Application (year and m³)		Fert.	Cult.	Plant Growth	
					1986	1987
1N	82,84	2.7 + 6	Low	High	Poor	Fair
1S	82,83,84	2.7 + 2.7 + 6	Low	High	Poor	Fair
2N	82,84	5.4 + 6	High	Low	V.Poor	Fair
2S	82,83,84	5.4 + 5.4 + 6	High	Low	V.Poor	Fair
3N	82,84	2.7 + 6	High	High	V.Poor	Poor
3S	82,83,84	2.7 + 2.7 + 6	High	High	V.Poor	Poor
4N	82,84	2.7 + 6	Low	Low	Poor	Fair
4S	82,83,84	2.7 + 2.7 + 6	Low	Low	Poor	Fair
5N	82,84	5.4 + 6	High	High	V.Poor	Fair
5S	82,83,84	5.4 + 5.4 + 6	High	High	V.Poor	Poor
6N	82,84	2.7 + 6	High	Low	Poor	Fair
6S	82,83,84	2.7 + 2.7 + 6	High	Low	Poor	Fair
7N	82,84	5.4 + 6	Low	Low	Poor	Fair
7S	82,83,84	5.4 + 5.4 + 6	Low	Low	V.Poor	Poor
8N	82,84	5.4 + 6	Low	High	Poor	Fair
8S	82,83,84	5.4 + 5.4 + 6	Low	High	V.Poor	Poor
Control	None		None	None	Fair	Fair

occurred in five of the southern plots which had received heavy applications of sludge. The poor growth may have been more related to the lack of establishement in 1986 rather than current levels of oil in the soil. Considerations should be given to either abandoning this site or replanting in 1988.

5.3.1.4 Plant growth at Brooks. Of the three species planted in 1986 at Brooks only crested wheatgrass was observed in 1987. Russian wild rye and sainfoin had not survived into the second growing season. Growth of crested wheatgrass was patchy indicating that establishment was limiting coverage rather than current oil contents. Weeds presented some problems throughout the area. In both plots 8S and 8N, kochia formed very dense stands and no evaluation of the crop was possible. Large Russian thistles were present between most plots and large plants were scattered on most of the north plots. Deadly nightshade and a few other weeds were also present, but not in sufficient quantity to interfere with crop growth.

Growth of crested wheatgrass was generally good in all the south plots which had received a single application of sludge in 1983 (Table 10). In contrast, growth was sparse in most of the north plots which received additional sludge in 1984. In the north plots receiving the low level of sludge there were a few scattered large Russian thistles and crested wheatgrass plants indicating that initial establishment in 1986 limited plant cover. In the plots treated with the largest amounts of sludge (1N, 4N, 5N, 7N) there were very few plants present.

5.3.2 Quantitative Estimates of Barley Growth at Lloydminster

Estimates of growth on plots 1W, 1E, 2W, 2E, 3W and 3E was not possible due to crop losses experienced in July. In the remaining plots, yields were generally low except in plot 8W in which growth was comparable to that found on the control area (Table 11). A comparison of the yields obtained in 1986 on the five replicate samples of plot 8 with the 1987 yields on samples taken from the same five sample points showed that growth was almost exactly the same in the two years. Yields ranged from 89 to 737 g m^{-2} in 1987 and from 104 to

Table 10. Visual estimates of plant growth of dryland pasture (primarily crested wheatgrass) on the Brooks landtreatment site (October 9, 1987) compared with 1986 results.

Plot	Sludge Application (year and m³)		Fert.	Cult.	Plant Growth	
					1986	1987
1S	83	5.6	Low	Low	Poor	Good
1N	83, 84	5.6 + 2.9	Low	Low	V.Poor	V.Poor
2S	83	2.8	High	High	Fair	Good
2N	83, 84	2.8 + 2.9	High	High	V.Poor	V.Poor
3S	83	2.8	Low	Low	Fair	Good
3N	83, 84	2.8 + 2.9	Low	Low	V.Poor	Good
4S	83	5.6	Low	High	Poor	Good
4N	83, 84	5.6 + 2.9	Low	High	V.Poor	V.Poor
5S	83	5.6	High	Low	Poor	Good
5N	83, 84	5.6 + 2.9	High	Low	V.Poor	V.Poor
6S	83	2.8	Low	High	Poor	Good
6N	83, 84	2.8 + 2.9	Low	High	V.Poor	Poor
7S	83	5.6	High	High	V.Poor	Fair
7N	83, 84	5.6 + 2.9	High	High	V.Poor	V.Poor
8S	83	2.8	High	Low	Poor	Dense Kochia
8N	83, 84	2.8 + 2.9	High	Low	V.Poor	Dense Kochia
Control		None	None	None	Fair	Good

Table 11. Yield of barley grown on soil treated with oily sludges and an adjacent untreated field at Lloydminster.

Plot	Sludge Application[1] (m^3)	Grain	Straw ($g \cdot m^{-2} \pm SD$)	Total
1W	4.2 + 1.6 + 2.3	ND[2]	ND	ND
2W	8.4 + 1.6 + 2.3	ND	ND	ND
3W	8.4 + 1.6 + 2.3	ND	ND	ND
4W	4.2 + 1.6 + 2.3	55 ± 46	69 ± 82	126 ± 129
5W	8.4 + 1.6 + 2.3	18 ± 14	7 ± 8	21 ± 21
6W	4.2 + 1.6 + 2.3	20 ± 8	15 ± 9	35 ± 14
7W	4.2 + 1.6 + 2.3	31 ± 17	35 ± 27	69 ± 48
8W	4.2 + 1.6 + 2.3	159 ± 101	236 ± 169	403 ± 272
1E	4.2 + 5.7 + 1.6 + 2.3	ND	ND	ND
2E	8.4 + 11.4 + 1.6 + 2.3	ND	ND	ND
3E	8.4 + 11.4 + 1.6 + 2.3	ND	ND	ND
4E	8.4 + 5.7 + 1.6 + 2.3	11 ± 4	5 ± 2	16 ± 5
5E	8.4 + 11.4 + 1.6 + 2.3	5 ± 3	1 ± 1	6 ± 3
6E	4.2 + 5.7 + 1.6 + 2.3	12 ± 3	3 ± 2	17 ± 4
7E	4.2 + 5.7 + 1.6 + 2.3	13 ± 3	4 ± 2	17 ± 5
8E	8.4 + 11.4 + 1.6 + 2.3	10 ± 5	1 ± 1	11 ± 6
Control	None	380 ± 54	251 ± 30	634 ± 87

[1] Sludge applied in 1982, 1983, and 1985 on west plots and an additional application in 1983 on the east plots.

[2] ND = not determined due to crop loss

727 g m^{-2} in 1986 with an average yield ratio between 1986 and 1987 of 1.01. In that the yields in plot 8W were so very similar in the two years, projected 1987 yields on plot 1W were calculated and used for oil content - productivity relationships between 1986 and 1987 yields on the same sample points indicate that the within plot variation was due to variations in soil chemistry and not to planting artifacts.

5.3.3 Soil Analyses

Extractable Ca, Mg, Na, Cl, and SO_4 were higher in all the sludge treatments than in the control soil (Table 12). In general, both total extractable cations and anions were lower in plots 6W, 7W, and 8W than in the other west plots. Salt concentrations were, in general, no higher in the east plots which had received additional sludge in 1983 than in the west plots. Chloride concentrations were highest in plots 1W, 2W, 3W, 4W, 5W, and 5E and did not appear to be related to overall sludge rate applications. Both Na and Cl concentrations were lowest in plots 7W, 8W, 7E and 8E. The soil pH was greater than 7.0 in all the plots and the control area and ranged up to pH 7.7 (Table 13). The electrical conductivity (E.C.) was greater in all the plots than the control area and within the plots was lowest in the plots 8W and 8E with the central plots tending to have higher values than the end plots. The sodium absorption ratios were also elevated in the plots as compared to the control soil and total carbon contents were about 3-fold higher in the treated plots than in the control soil.

All the major cations and anions were in greater concentrations in the surface 2 cm of soil than in the 0-10 cm layer (Table 14). Chloride, Na and SO_4 concentrations in the surface soil in plots 5W and 7W were about twice that found in the bulk soil. In plot 8W ionic concentrations were low in both the bulk and surface woil. Electrical conductivity was substantially higher in the surface 2 cm than in the bulk soil in all three plots, but the sodium absorption ratio was similar in both depths sampled (Table 15).

In the transect across the end of plot 8, plant growth showed an increase in productivity from poor to good but the oil content was relatively higher in all the samples, ranging from 3.8 to 5.9% (Table 16). Total C contents were also well above the control value of

Table 12. Cation and anion concentrations in saturated extracts of soils treated with oily sludges at Lloydminster, sampled October 2, 1987.

Plot	Sludge	Fert	Ca	Mg	Na	K	NH_4-N	NO_3-N	Cl	SO_4	HCO_3
			m.e. L^{-1} ($\bar{x} \pm SD$)								
1W	Low	High	12.1 ± 1.0	4.3 ± 0.5	15.5 ± 2.2	0.21 ± .01	0.11 ± .01	0.63 ± 0.96	16.9 ± 2.4	6.6 ± 1.3	6.2 ± 0.4
2W	Med	Low	15.7 ± 3.2	6.0 ± 1.3	23.5 ± 8.7	0.22 ± .04	0.13 ± .02	0.08 ± 0.08	21.1 ± 12.0	13.7 ± 1.5	6.7 ± 0.5
3W	Low	High	16.9 ± 2.8	6.0 ± 1.1	16.0 ± 2.3	0.21 ± .01	0.09 ± .01	0.02 ± 0	17.8 ± 4.7	12.3 ± 2.0	5.9 ± 0.3
4W	Low	High	21.0 ± 7.8	7.1 ± 2.6	19.2 ± 6.9	0.27 ± .05	0.10 ± .01	1.62 ± 1.57	27.5 ± 13.1	11.0 ± 2.3	5.2 ± 0.1
5W	Med	Low	18.0 ± 3.5	5.8 ± 1.2	15.6 ± 4.3	0.25 ± .02	0.09 ± .01	0.02 ± 0.01	17.3 ± 7.4	13.0 ± 2.2	5.9 ± 0.3
6W	Low	High	13.9 ± 0.8	4.1 ± 0.4	11.6 ± 1.7	0.19 ± .01	0.10 ± .01	0.18 ± 0.04	9.5 ± 1.9	11.2 ± 0.7	5.7 ± 0.4
7W	Low	Low	11.2 ± 1.4	3.7 ± 0.5	7.4 ± 1.8	0.14 ± .01	0.10 ± .01	0.17 ± 0.06	4.9 ± 1.3	8.5 ± 2.0	6.2 ± 0.6
8W	Med	High	8.8 ± 1.2	2.8 ± 0.4	5.4 ± 1.4	0.16 ± .02	0.09 ± .01	0.03 ± 0.01	3.9 ± 1.7	4.7 ± 1.4	6.5 ± 0.2
1E	Med	Low	9.9 ± 2.5	3.8 ± 1.0	12.8 ± 2.0	0.19 ± .02	0.09 ± .01	0.73 ± 1.60	10.9 ± 4.7	5.8 ± 0.8	6.4 ± 0.4
2E	High	High	7.6 ± 3.4	4.2 ± 0.6	10.9 ± 1.3	0.18 ± .01	0.09 ± .01	0.05 ± 0	6.6 ± 1.8	7.8 ± 1.0	6.9 ± 0.3
3E	High	Low	11.2 ± 2.0	4.9 ± 0.9	13.7 ± 2.7	0.20 ± .01	0.09 ± .01	0.01 ± 0	9.2 ± 4.1	9.9 ± 1.0	7.0 ± 0.2
4E	Med	High	16.7 ± 3.1	6.1 ± 1.5	13.9 ± 4.1	0.25 ± .04	0.12 ± .01	0.01 ± 0	14.0 ± 6.6	11.7 ± 1.6	7.4 ± 0.6
5E	High	Low	19.6 ± 2.7	8.6 ± 1.2	21.5 ± 2.9	0.22 ± .02	0.14 ± .02	0.02 ± 0	22.4 ± 4.9	13.8 ± 2.3	8.5 ± 0.4
6E	Med	High	13.9 ± 3.8	5.5 ± 1.6	14.3 ± 5.4	0.20 ± .03	0.11 ± .01	0.02 ± 0	12.6 ± 8.1	10.1 ± 2.5	7.7 ± 0.3
7E	Med	Low	15.7 ± 2.4	5.6 ± 0.9	13.5 ± 2.1	0.18 ± .01	0.06 ± .01	0.02 ± 0	10.2 ± 3.8	12.1 ± 1.6	8.2 ± 0.4
8E	High	High	12.3 ± 5.0	3.8 ± 0.4	7.4 ± 1.5	0.15 ± .02	0.02 ± 0	--	2.4 ± 0.8	8.0 ± 1.0	7.9 ± 0.4
Control	--	--	6.5 ± 0.3	2.2 ± 0.2	0.6 ± 0.1	0.40 ± .11	0.33 ± .39	0.32 ± 0.44	0.2 ± 0	0.7 ± 0.1	8.1 ± 0.3

Table 13. Soil pH, electrical conductivity, and sodium adsorption ratio of Lloydminster plots treated with oily sludge.

Plot	Sludge	Fert.	pH	E.C. ($ds\ m^{-1}$)	S.A.R.	Total Carbon
			($\bar{x} \pm SD$)			
1W	Low	Low	7.2 ± 0.6	3.0 ± 0.2	5.4 ± 0.6	5.1 ± 0.4
2W	Med	high	7.4 ± 0.1	4.0 ± 1.3	7.1 ± 2.1	6.4 ± 0.7
3W	Med	Low	7.4 ± 0.1	3.5 ± 0.5	4.7 ± 0.4	5.6 ± 0.2
4W	Low	High	7.4 ± 0.1	4.3 ± 1.6	4.0 ± 1.0	5.0 ± 0.4
5W	Med	Low	7.4 ± 0.1	3.4 ± 0.8	4.5 ± 0.9	6.1 ± 0.8
6W	Low	High	7.3 ± 0.1	2.5 ± 0.1	3.9 ± 0.6	6.1 ± 0.4
7W	Low	Low	7.5 ± 0.3	1.9 ± 0.3	2.7 ± 0.5	6.3 ± 0.7
8W	Med	High	7.7 ± 0.1	1.4 ± 0.3	2.0 ± 0.6	5.5 ± 0.3
1E	Med	Low	7.7 ± 0.1	2.4 ± 0.5	4.9 ± 0.2	5.6 ± 0.5
2E	High	High	7.6 ± 0.1	2.0 ± 0.2	4.1 ± 0.5	6.4 ± 0.5
3E	High	Low	7.6 ± 0.1	2.5 ± 0.5	4.8 ± 0.5	6.3 ± 0.2
4E	Med	High	7.2 ± 0.2	3.1 ± 0.8	4.1 ± 0.8	6.8 ± 0.5
5E	High	Low	7.0 ± 0.1	4.3 ± 0.6	5.7 ± 0.4	7.0 ± 0.5
6E	Med	Low	7.2 ± 0.1	2.9 ± 1.0	4.5 ± 1.0	5.9 ± 0.5
7E	Med	Low	7.1 ± 0.1	2.9 ± 0.5	4.2 ± 0.3	6.9 ± 0.5
8E	High	High	7.0 ± 0.2	1.7 ± 0.2	2.6 ± 0.3	7.2 ± 0.8
Control	--	--	7.6 ± 0.2	0.8 ± 0.1	0.3 ± 0.1	2.1 ± 0.3

Table 14. Cation and anion concentrations in saturated extracts of the 0-2 and 0-10 cm depths of soils from three plots treated with oily sludges.

Plot	Soil Depth (cm)	Ca	Mg	Na	K	NH_4-N	NO_3-N	Cl	SO_4	HCO_3
		m.e. L^{-1} ($\bar{x} \pm SD$)								
5W	0-2	45 ± 11	15 ± 2	30 ± 14	0.38 ± .06	0.37 ± .19	0.07 ± .14	40 ± 24	35 ± 14	11 ± 1
5W	0-10	18 ± 3	6 ± 1	16 ± 4	0.25 ± .02	0.09 ± .01	0.02 ± .01	17 ± 7	13 ± 2	6 ± 1
7W	0-2	26 ± 9	7 ± 3	12 ± 6	0.25 ± .03	0.24 ± .03	0.01 ± .01	12 ± 7	18 ± 6	11 ± 1
7W	0-10	11 ± 1	3 ± 1	7 ± 2	0.14 ± .01	0.10 ± .01	0.17 ± .06	5 ± 1	8 ± 2	6 ± 1
8W	0-2	15 ± 3	5 ± 2	4 ± 2	0.33 ± .05	0.27 ± .04	0.01 ± .01	6 ± 4	5 ± 3	11 ± 1
8W	0-10	9 ± 1	3 ± 1	5 ± 1	0.16 ± .02	0.09 ± .01	0.03 ± .01	4 ± 2	5 ± 1	6 ± 1

Table 15. Soil pH, total carbon, electrical conductivity, and sodium adsorption ratio of the 0-2 and 0-10 cm depths from three plots treated with oily sludge.

Plot	Soil	pH	E.C. (ds m^{-1})	S.A.R.	Total Carbon
		($\bar{x}$ ± SD)			
5W	0-2	7.1 ± 0.1	7.0 ± 2.7	5.5 ± 2.0	6.7 ± 0.8
5W	0-10	7.1 ± 0.1	3.4 ± 0.8	4.5 ± 0.9	6.1 ± 0.8
7W	0-2	7.1 ± 0.1	3.7 ± 1.2	2.7 ± 0.9	7.0 ± 0.2
7W	0-10	7.5 ± 0.3	1.9 ± 0.3	2.7 ± 0.5	6.3 ± 0.7
8W	0-2	7.2 ± 0.1	2.1 ± 0.6	1.5 ± 0.5	5.9 ± 0.5
8W	0-10	7.7 ± 0.1	1.4 ± 0.3	2.0 ± 0.6	5.5 ± 0.4

Table 16. Soil chemical characteristics of five adjacent 1 m² locations on a transect in which plant growth ranged from poor to good.

Sample	Whole Plant (g)	Grain Weight (g)	Oil Content (%)	Total Carbon (%)	E.C.	S.A.R.	Na	Cl	SO_4
					ds m^{-1}		m.e. L^{-1}		
81	41	15	5.0	6.4	1.7	3.1	7.8	3.0	7.1
82	113	56	5.9	6.8	1.6	2.5	6.5	2.0	7.1
83	246	131	4.9	6.6	1.4	2.3	5.5	1.5	5.9
84	269	212	4.1	6.3	1.2	1.8	4.3	1.4	3.9
85	523	321	3.8	5.8	1.3	1.8	4.4	2.1	4.3

2.1%. The E.C., SAR and concentrations of Na, Cl and SO_4 were all greater in the poor growth plots than in the good growth plots, but the values did not appear to be excessive for any of the parameters measured.

Potentially toxic metals were measured in four plots exhibiting poor to good growth and in the control soil (Table 17). In general, metal concentrations were higher in the treated soils but differences were relatively small.

5.3.4 Heavy Metal Content of Barley

Concentrations of all the metals in both grain and straw were not elevated in plants grown in sludge-treated soils as campared to the controls with the exception of Fe (Table 18). Fe was found in higher concentrations in the straw than in the grain and was exceptionally high in plants from plot 6W. These plants were stunted and would not be normally harvested. Concentrations of Fe in plants from plot 8W were similar to plants grown in the control soil.

5.3.5 Plant Growth in the Greenhouse

Barley grew relatively well in all the soils from the Lloydminster west plots (Table 19). Growth was marginally better in soils from plots 1W, 8W and the control area but there did not appear a clear relationship between sludge application and productivity in the greenhouse or between growth in the field in the greenhouse. Nearly all the plants grown on sludge-treated soils were strongly chlorotic after 5 weeks whereas the plants in the control remained dark green.

The alsike clover grew much better in the control soil than in any of the oil-treated soils and growth was substantially better in soil from plots 1W and 8W than in soil from the other plots (Table 19). Growth of clover appeared to be directly related to the amounts of sludge applied in the field and reflected the growth of barley in the field. No chlorosis of the clover was evident but some leaves of all the plants grown in the oil-treated soils exhibited a narrow white border whereas all the leaves of plants in the control soil were healthy.

Table 17. DTPA extractable metals from Lloydminster soils treated with oily sludges.

Plot	Fe	Cu	Zn	Pb	Mn	Cd	Ni
	mg kg^{-1}						
4W	34 ± 5	0.51 ± 0.04	1.7 ± 0.1	1.7 ± 0.5	6.4 ± 0.5	0.07 ± .01	0.8 ± .02
6W	38 ± 10	0.60 ± 0.02	1.9 ± 0.1	1.5 ± 0.2	8.3 ± 1.2	0.06 ± .01	0.9 ± .04
7W	42 ± 4	0.55 ± 0.02	1.7 ± 0.2	1.4 ± 0.1	8.3 ± 2.1	0.05 ± .01	0.9 ± .03
8W	32 ± 1	0.58 ± 0.10	2.0 ± 0.1	1.4 ± 0.3	5.2 ± 0.5	0.08 ± .01	0.9 ± .02
Control	26 ± 2	0.31 ± 0.01	0.6 ± 0.1	0.5 ± 0.1	3.2 ± 0.1	0.04 ± 0	0.7 ± .04

Table 18. Heavy metal contents of barley straw and grain grown in oil-free and oily sludge treated soil at Lloydminster.

Plot		Fe	Cu	Zn	Pb	Mn	Cd	Ni
		mg kg^{-1}						
Control	grain	45 ± 18	6 ± 3	23 ± 4	7 ± 2	17 ± 1	<1	11 ± 12
Control	straw	58 ± 11	3 ± 1	8 ± 2	3 ± 1	15 ± 2	<1	3 ± 1
6W	grain	150 ± 100	4 ± 2	18 ± 2	6 ± 2	40 ± 7	<1	5 ± 4
6W	straw	910 ± 192	3 ± 2	11 ± 1	3 ± 1	81 ± 11	<1	5 ± 1
8W	grain	14 ± 19	4 ± 2	30 ± 11	10 ± 3	26 ± 2	<1	7 ± 4
8W	straw	197 ± 131	2 ± 1	13 ± 3	<2	46 ± 6	<1	1

Table 19. Growth of Leduc variety barley and alsike clover grown in the greenhouse on soils previously treated with oily sludges at Lloydminster.

Field Treatment						
Plot	Sludge	Fert	Crop Yield ($g \cdot m^{-2}$)	Barley Plants in 5 Pots[3]	Barley ($g \cdot pot^{-1} \pm SD$)	Clover
1W	Low	Low	ND[2]	47	0.75 ± 0.12	0.32 ± 0.06
2W	Med	High	ND	38	0.57 ± 0.16	0.13 ± 0.08
3W	Med	Low	ND	37	0.59 ± 0.20	0.14 ± 0.05
4W	Low	High	126	46	0.67 ± 0.14	0.10 ± 0.02
5W	Med	Low	21	37	0.53 ± 0.06	0.09 ± 0.07
6W	Low	High	35	40	0.59 ± 0.08	0.15 ± 0.09
7W	Low	Low	69	37	0.42 ± 0.08	0.13 ± 0.07
8W	Med	High	403	42	0.71 ± 0.18	0.32 ± 0.13
Control	None	--	674	33[4]	1.35 ± 0.13	1.09 ± 0.14

[1] See Table 7 for exact rates

[2] ND = not determined due to loss of crop

[3] Ten seeds planted per pot, five pots per treatment

[4] Number of plants in four pots

5.4 DISCUSSION

Growth of the perennial crops at Drayton Valley, Grande Prairie, and Brooks all improved in the second growing season. Good growth occurred on all three areas, although some plots receiving heavy sludge applications were still bare. However, it appeared that even most of the barren areas would support reasonable crop growth as there were widely scattered, healthy plants on nearly all plots. Thus the problem appeared to be the lack of initial establishment rather than current sludge levels in the soil.

At Lloydminster, plant growth was very similar to that observed in 1986. The difference between Lloydminster and the other three sites is probably due to the additional sludge applications at Lloydminster and the quality of the sludges. The sludge applied at Lloydminster contained significant quantities of salts which may have influenced plant growth. The electrical conductivity of some samples exceeded 4 $ds \cdot m^{-1}$ which is high enough to inhibit plant growth (Brady 1974). Plots in which good growth occurred had electrical conductivities of less than 4 $ds \cdot m^{-1}$. Salts were more concentrated in the surface soil which may have adversely influenced root development and initial plant establishment.

In the greenhouse, sludge-treated soils inhibited both the growth of barley and clover in all treatments. As observed previously (Danielson et al. 1987), the legume was more sensitive than the grass. The chlorotic nature of the barley suggests that nitrogen may be limiting plant growth due to its utilization by sludge decomposing organisms. The quantity of available nitrogen was less in the sludge-treated soil than in the control soil, again indicating that nitrogen could be limiting plant growth. In the future, nitrogen fertilization in the plots should be increased over the levels being used in the adjacent field.

6. RELATIONSHIP BETWEEN PLANT PRODUCTIVITY AND SOIL CHEMISTRY

Oil contents were measured at 5 sampling points within each of the 16 subplots at the Lloydminster site. The results for the 5 replicates from each subplot were averaged, yielding a total of 16 characteristic oil contents. The growth of barley was first assessed visually (before quantifications were made) and these two sets of data are combined with details of the magnitude of the sludge and fertilizer treatment and presented in a simplified representation of the Lloydminster site in Figure 2. Sludge applications were ranked as low (L), medium (M), or high (H), while fertilizer applications were classified as either high (H) or low (L). Growth assessments were abbreviated accordingly; G, good; F, fair; P, poor; and VP, very poor. The growth assessments included in Plots 1 (E and W) and 2 (E and W) were assumed to be the same as last year since the crops in these 2 plots had been accidentally cut. Since the 1987 growth in the other plots paralleled the previous year's, this assumption is not unreasonable.

The weights of dried barley can be matched to the oil content of the soil in which it was grown. Plant material was collected within each subplot at the same 4 sampling points that the oil content were measured. The information from each sampling point (rather than averaged values) is shown in Figure 3. Although this illustration closely resembles the one derived from last year's data, 4 points are markedly different. These are distinguished from the other points in Figure 3 by 2 concentric circles, and are representative of some additional sampling points along the border of Plot 8 where growth showed an obvious gradient (see Table 16). Five other points are distinguished by unfilled circles since these symbolize estimated growth based on last year's patterns (See Section 5.3.2).

The relationship between plant weight and oil content reveals a great degree of scatter; however, the trend of decreasing productivity with increasing oil content is self-evident. This dependency becomes more obvious if the plots are grouped according to their observed growth (as opposed to measured growth) and the oil contents of those plots exhibiting roughly the same growth are averaged, then a simplified diagram showing an approximate relationship between growth

sludge application	fertilizer application
oil : solids ratio	growth

	East		West	
Plot 1	M 2.72	L G	L 2.13	L G
Plot 2	H 4.67	H F	M 4.91	H P
Plot 3	H 5.35	L P	M 4.25	L F
Plot 4	M 5.96	H P	L 2.88	H F-G
Plot 5	H 6.71	L VP	M 4.58	L P-F
Plot 6	M 4.97	H P-F	L 4.39	H F
Plot 7	M 6.15	L P	L 4.53	L P-F
Plot 8	H 6.97	H VP	M 3.05	H G

L-low ; M - medium ; H-high

G-good ; F - fair ; P - poor ; VP-very poor

Figure 2. An overall view of the sludge and fertilizer application, oil content, and growth assessment at the Lloydminster site.

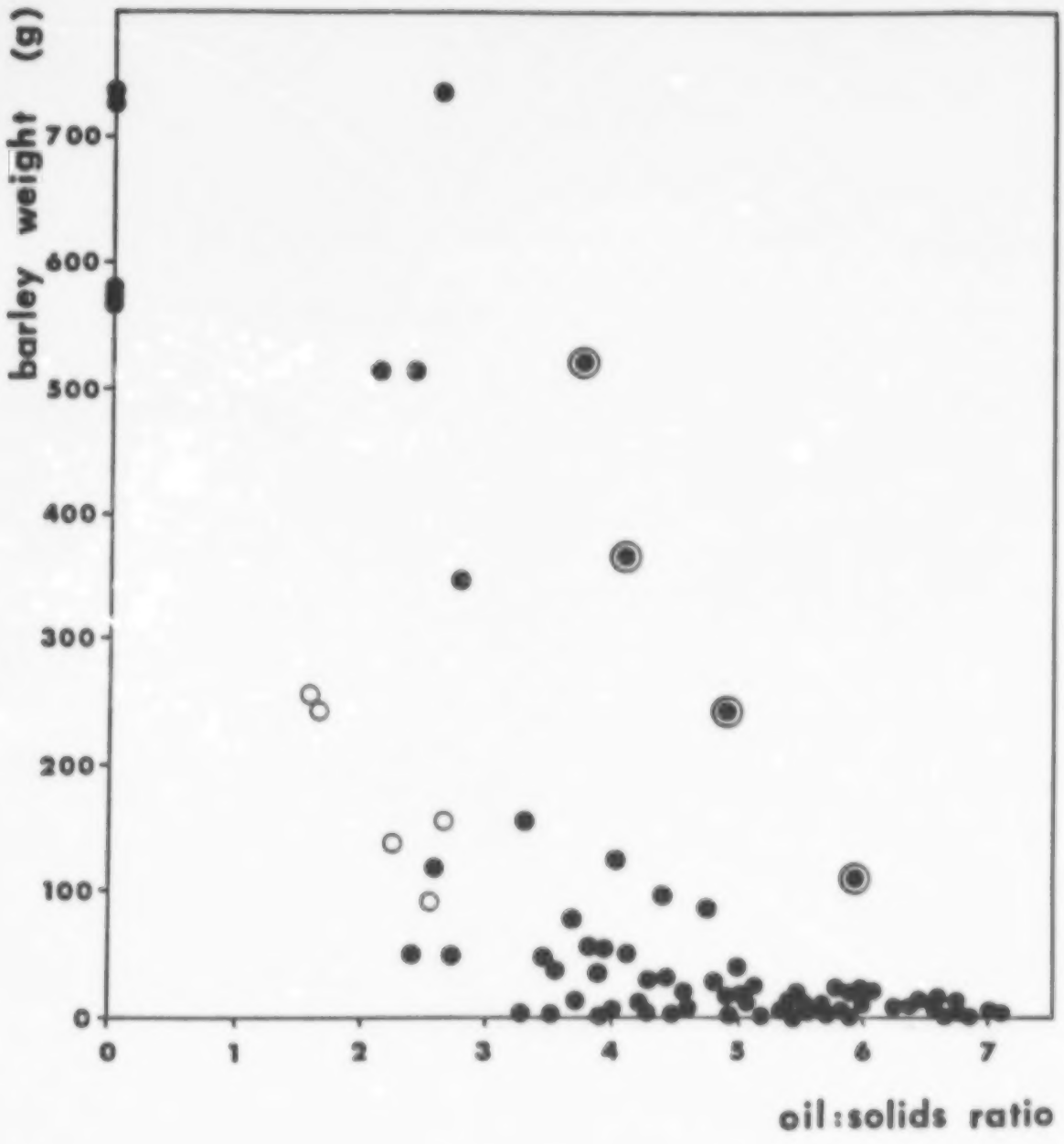


Figure 3 Dependency of plant productivity on the corresponding oil content of the soil at the Lloydminster site.

and oil content can be created. Figure 4 displays this correlation for growth at the Lloydminster site. When compared to the same correlation drawn using 1986 data, the slope of the line is unchanged although the data points for 1987 are consistently lower. The range of oil content values has also decreased substantially.

Last year a set of oil content ranges were proposed as guidelines for expected productivity. Good growth was generally observed when the oil content of the soil was below 3.5%, fair growth between 3.5 and 5%, and poor growth in excess of 5%. This year these ranges have been slightly altered. An additional correlation was prepared since cut-off points were not obvious in Figures 2 or 3. In Figure 5, plant weights were averaged rather than using individual values as in Figure 3. Plant weights were grouped according to ranges of oil contents (i.e., average weights of barley raised on soils having oil contents between 2 and 2.5%, 2.5 and 3.0%, etc., were calculated). There is a gap in Figure 5 between the control weights (inserted between 0 and 0.5%), and those corresponding to the lowest oil contents; this came about for the simple reason that none of the plots had oil contents lower than 1.5%. This graph, however, exhibits 3 distinct regions of growth: one from 0 to 3%, another from 3 to 5%, and a third above 5%. These 3 ranges typify regions of good, fair, and poor growth, respectively.

Concern is usually expressed over the presence of asphaltenes in the soil, and whether this component of the oil is the most detrimental to growth. The asphaltene content of the soil was matched with the visual growth assessment for each subplot of the Lloydminster site, and Figure 6 was generated. The correlation is actually a smooth one considering the subjective nature of the growth classifications. It appears that good growth occurs when the asphaltene content is below 0.6%, fair growth between 0.6 and 0.96%, and poor growth above 0.96%. Whether oil content or asphaltene content is the factor better able to predict growth is unknown.

In 1986 it appeared that salt concentrations could also be a factor in limiting plant growth and thus, salt concentrations were measured in all the plots and in the five samples from the border of plot B in which a growth gradient was observed. Salt concentrations

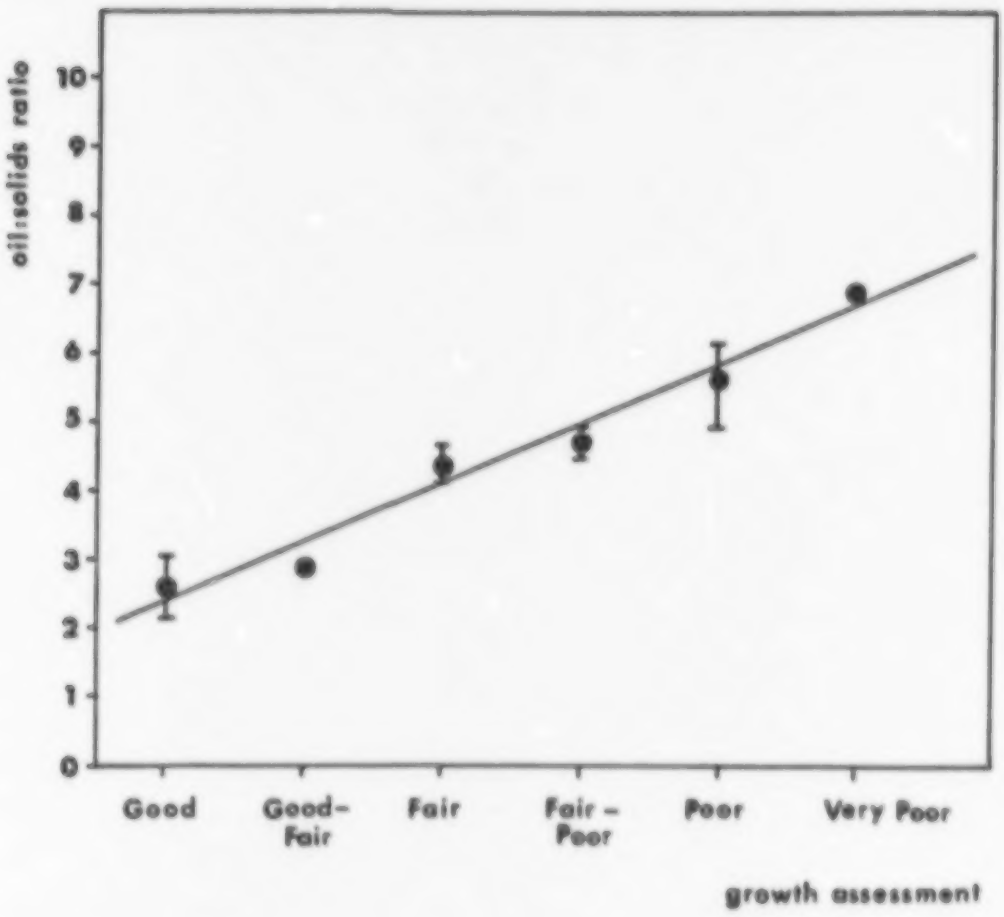


Figure 4. Approximate correlation between observed growth of barley and soil oil content at the Lloydminster site. Bars indicate the range of values.

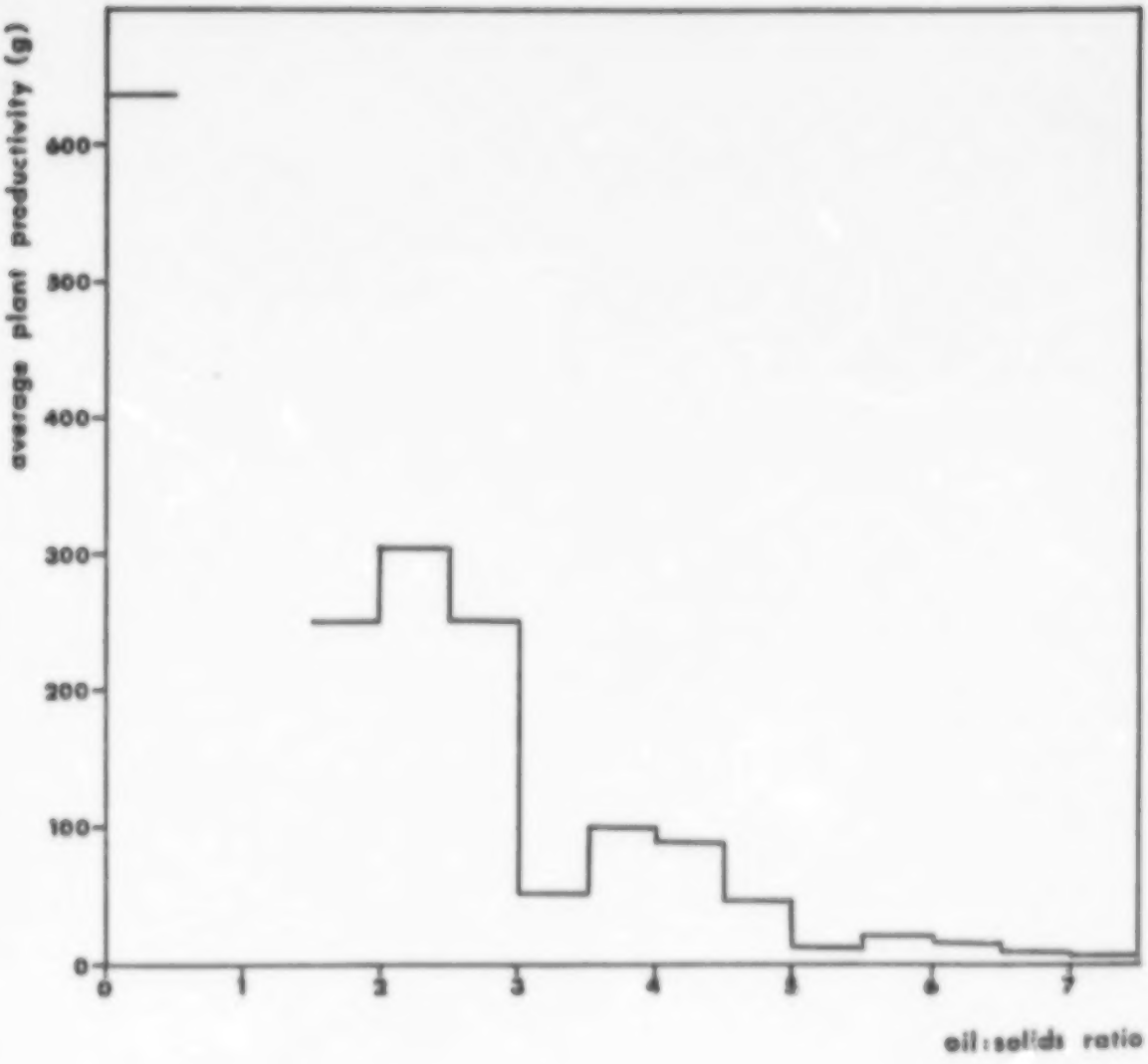


Figure 5. Relationship between average growth and oil content (grouped into 0.5% ranges).

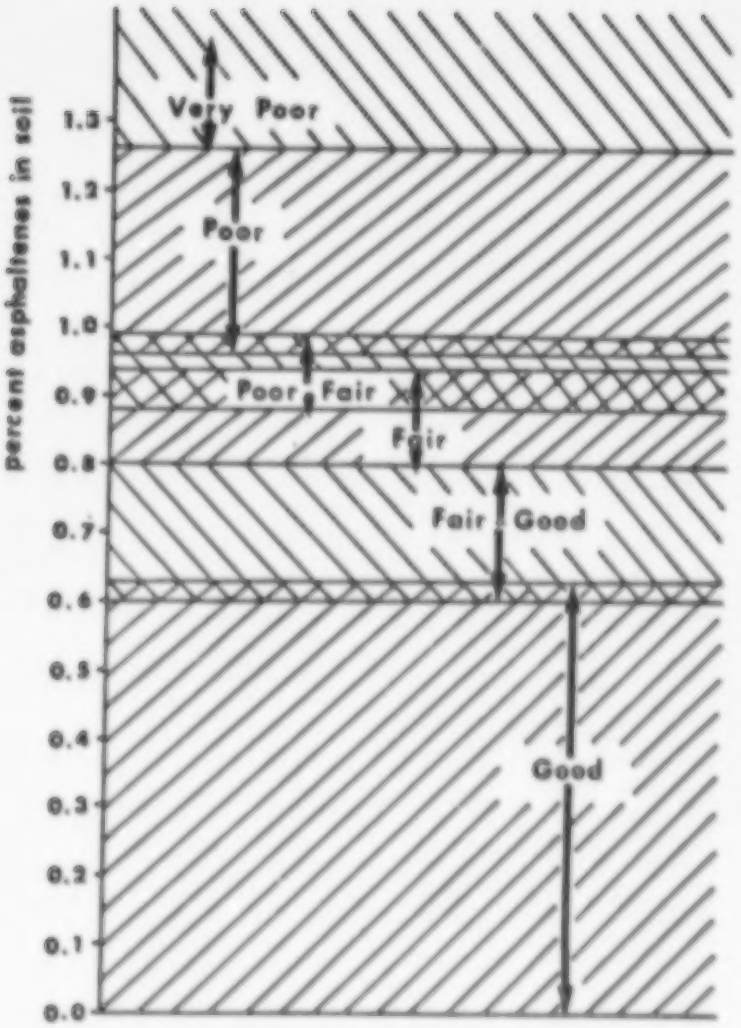


Figure 6. Relationship between asphaltene content in the soil and the observed growthy of barley at the Lloydminster site.

were generally lowest in the plots demonstrating the best growth (1W, 1E, and 8W). There was no clear correlation between total sludge applied and salt concentrations, suggesting that differences must have existed among the individual loads of sludge that were applied. Nonetheless, it appears that salts were adversely affecting plant growth as electrical conductivities of saturated extracts of soils supporting good growth were almost always low. The data points on Figure 3 that are above 150 $g \cdot m^{-2}$ do not exceed conductivities above 2.9 $ds \cdot m^{-1}$ except in one instance.

There is apparently an interaction between oil content and salt concentration as when oil contents exceeded 3.5%, growth was nearly always poor and was also poor below this value if electrical conductivity exceeded 3 $ds \cdot m^{-1}$. On the plots exhibiting the best growth, 1W and 8W, growth was poorest where oil contents exceeded 3% or where salt concentrations were relatively high (Table 20). Salt concentrations were lowest (<1.6 $ds \cdot m^{-1}$) in the soils taken from the growth transect at the end of plot 8. In these samples, barley growth was moderately good even when oil content was as high as 4.9% (see Figure 3). It thus appears that if salt inputs are minimized in landtreatment sites, rehabilitation of the sites can be made more quickly.

Table 20 Comparison of barley yields, oil contents, and soil chemistry on plots 1W and 8W in 1986 and 1987.

	Barley yield $g\ m^{-2}$		Oil Content %		E.C. $ds \cdot m^{-1}$		SAR		Cl m.e. L^{-1}	
Sample	1986	1987	1986	1987	1986	1987	1986	1987	1986	1987
36	173	158	3.8	3.3	-	1.7	-	2.7	-	5.0
37	537	515	3.3	2.1	1.2	1.7	2.8	1.2	3.5	6.1
38	727	737	2.3	2.6	1.3	1.3	2.2	2.0	3.8	3.6
39	104	89	4.8	4.7	1.3	1.5	2.7	2.3	1.6	3.2
40	379	514	2.7	2.4	1.4	1.0	2.5	1.6	4.3	1.6
1	246	243[1]	2.4	1.6	1.8	2.9	4.5	5.2	8.5	16.2
2	165	158[1]	2.8	2.6	2.5	2.6	5.5	4.7	14.0	13.2
3	139	138[1]	2.9	2.2	3.4	3.2	7.2	6.3	19.8	17.5
4	259	256[1]	1.9	1.6	3.4	2.9	6.2	5.0	21.8	18.7
5	93	92[1]	3.0	2.5	3.2	3.2	7.2	5.7	17.3	19.2

[1] Yields estimated based on a 1% yield reduction in plot 8 between 1986 and 1987.

7. GROUNDWATER AND SURFACE WATER

7.1 OBJECTIVES

The Earth Sciences Division is conducting a hydrogeological investigation of the land treatment plots to establish directions of shallow groundwater flow, shallow groundwater chemistry, and to assess the impact of land treatment on groundwater quality. Surface waters are also sampled to determine if sludge or fertilizer is affecting runoff water quality.

This section of the report contains a discussion of 1986 and 1987 groundwater and surface water monitoring at the land treatment plots.

7.2 GEOLOGY

A total of 22 boreholes at eleven sites were drilled, using a solid stem auger system, to define the shallow geology beneath the plots. Drill cuttings were collected and described at 0.5 m intervals. At one location, a continuous core was collected to facilitate detailed description of geology and structure. Test hole locations are shown in Figure 7 and borehole logs and the core description are appended.

The site is underlain by fine textured till to a depth of at least 9 m. The till, grey, grading to grey-brown with depth, is dense, plastic and contains numerous pebbles and fine-grained sand lenses. Visual examination of the core from 493 suggests the presence of fractures to a depth of at least 2.5 m. The fracture faces are commonly coated with calcite and/or iron staining.

Fifteen piezometers and seven water table wells were subsequently installed in the boreholes. Two water table wells, W 331 and W 332, were constructed using stainless steel and teflon materials and equipped with dedicated sampling hoses. Completion details for installations are appended.

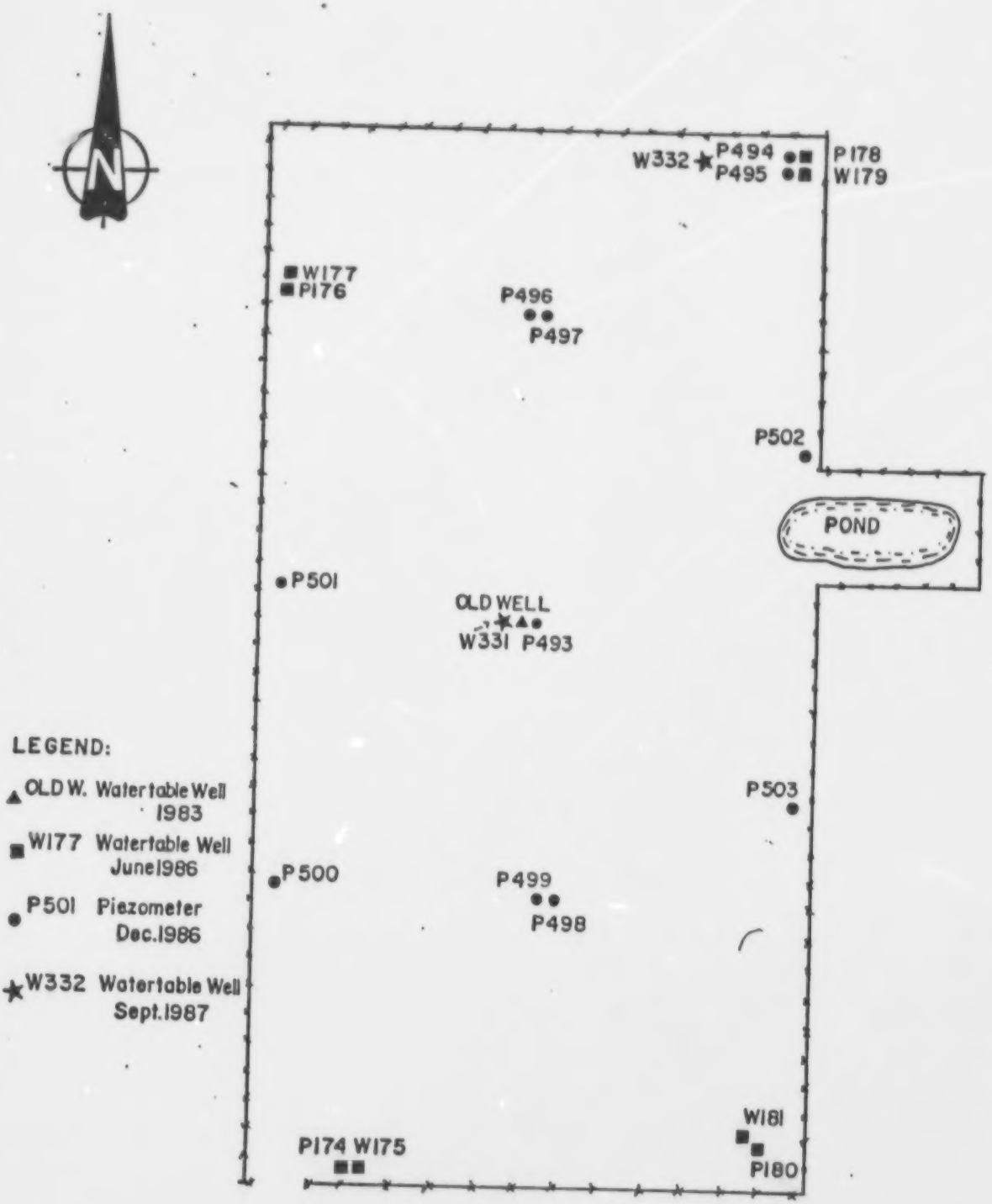


Figure 7. Site plan.

7.3 GROUNDWATER FLOW

Water levels have been recorded on ten occasions (Table 21). A water table contour map constructed using data obtained on February 19, 1987 (Figure 8), suggests that the predominant direction of shallow groundwater flow is toward the east under the influence of a shallow hydraulic gradient.

Water level data from the piezometer nest located in the northeast corner of the site indicate that the site is located in a groundwater recharge area. That is, the predominant direction of groundwater flow is downward. A vertical hydraulic gradient of 0.6 is estimated from available data.

Water levels in the water table wells reached a static equilibrium slowly after well installation. A noticeable increase in water levels was evident in late July - early August, 1986, and also in September 1987 (Figure 9). These increases are attributable to unusually high precipitation in June-July, 1986 and July-August 1987. Water levels tend to decrease in fall and winter due to a lack of recharge. The annual water table fluctuation is in the order of 1.5 m.

No hydraulic conductivity tests have been conducted on the piezometers. Consequently, accurate in-situ hydraulic conductivity (k) data for various geological materials beneath the site is not available. However, qualitative estiamtes of k are possible from a visual analysis of the core and from the length of time required for the water level in each monitor to reach equilibrium. Clayey textured till which is fractured or contains lenses of fine grained sand, is expected to have the highest k value, in the range 10^{-5} - 10^{-7} cm/sec. The lowest k values, approximately 10^{-8}, are characteristic of till generally deeper than 6 m from surface. Single well response tests are planned for 1988 to obtain quantitative information about in-situ k values. The data will be used to calculate shallow groundwater flow velocities.

Table 21. Water level data.

WELL NUMBER	86/06/09 DEPTH (t.o.c.) (m)	86/06/09 ELEV. (m)	86/07/03 DEPTH	86/07/03 ELEV.	86/07/22 DEPTH	86/07/22 ELEV.	86/08/12 DEPTH	86/08/12 ELEV.	86/09/09 DEPTH	86/09/09 ELEV.	86/12/03 DEPTH	86/12/03 ELEV.	87/01/06 DEPTH	87/01/06 ELEV.	87/02/10 DEPTH	87/02/10 ELEV.	87/09/02 DEPTH	87/09/02 ELEV.	87/12/01 DEPTH	87/12/01 ELEV.
old well	2.6	98.33	2.0	98.93	1.38	99.55	1.44	99.49	2.8	98.13	2.94	97.99*	3.52	97.41	----	----	2.00	98.39	2.58	98.35
p 174	dry	----	8.6	92.72	7.12	94.00	7.44	93.68	6.01	95.11	4.76	96.36*	4.84	96.28	6.08	95.04	3.94	97.18	5.66	95.46
w 175	dry	----	5.23	95.92	3.71	97.44	3.66	97.49	2.63	98.52	2.5	98.65*	2.67	98.48	3.45	97.70	1.98	98.20	3.03	97.15
p 176	dry	----	9.03	92.20	8.1	93.13	7.48	93.75	5.88	95.35	4.82	96.41*	4.68	96.55	6.17	95.06	4.09	97.14	5.07	96.16
w 177	dry	----	5.49	95.84	4.16	97.17	3.48	97.85	2.46	98.87	2.67	98.66*	4.99	96.34	3.33	98.00	2.86	98.47	3.71	97.62
p 178	6.6	94.41	5.49	95.52	5.25	95.76	4.76	96.25	5.02	95.99	5.57	95.44*	5.68	95.33	5.75	95.26	5.22	95.79	5.48	95.53
w 179	6.7	94.32	4.4	96.62	2.6	98.42	2.15	98.87	2.34	98.68	2.82	98.20*	2.99	98.03	3.78	97.24	2.87	98.15	3.92	97.10
p 180	7.83	93.35	2.92	98.26	2.42	98.76	2.06	99.12	2.58	98.60	2.93	98.25*	3.10	98.08	3.36	97.82	2.59	97.59	2.44	97.74
w 181	dry	----	5.47	95.64	4.51	96.60	3.96	93.15	2.83	98.28	2.82	98.29*	3.87	98.04	4.18	96.93	2.54	98.57	3.54	97.57
p 493	---	----	----	----	----	----	----	----	---	----	---	----	4.10	97.08	3.18	95.86	1.97	99.21	2.88	98.30
p 494	---	----	----	----	----	----	----	----	---	---	---	----	5.58	95.31	5.32	95.57	2.75	98.14	3.79	97.10
p 495	---	----	----	----	----	----	----	----	---	----	---	----	4.95	96.01	3.72	97.24	2.71	98.25	3.28	97.68
p 496	---	----	----	----	----	----	----	----	---	----	---	----	5.36	95.96	5.24	96.08	2.94	98.38	4.32	97.00
p 497	---	----	----	----	----	----	----	----	---	----	---	----	3.38	97.91	3.33	97.96	2.24	99.05	2.88	98.41
p 498	---	----	----	----	----	----	----	----	---	----	---	----	5.28	96.01	4.96	96.33	2.69	98.60	3.85	97.44
p 499	---	----	----	----	----	----	----	----	---	----	---	----	3.98	97.26	3.89	97.35	2.54	98.70	3.14	98.10
p 500	---	----	----	----	----	----	----	----	---	----	---	----	2.68	98.52	2.81	98.39	2.27	98.93	2.70	98.50
p 501	---	----	----	----	----	----	----	----	---	----	---	----	4.85	96.28	4.68	96.45	3.08	98.05	3.97	97.16
p 502	---	----	----	----	----	----	----	----	---	----	---	----	4.82	96.28	4.51	96.59	2.18	98.92	3.39	97.77
p 503	---	----	----	----	----	----	----	----	---	----	---	----	4.85	96.42	4.58	96.69	2.69	98.58	3.53	97.74
w 331																			3.16	97.49
w 332																			4.89	95.46

* Well bailed dry after water level recorded.

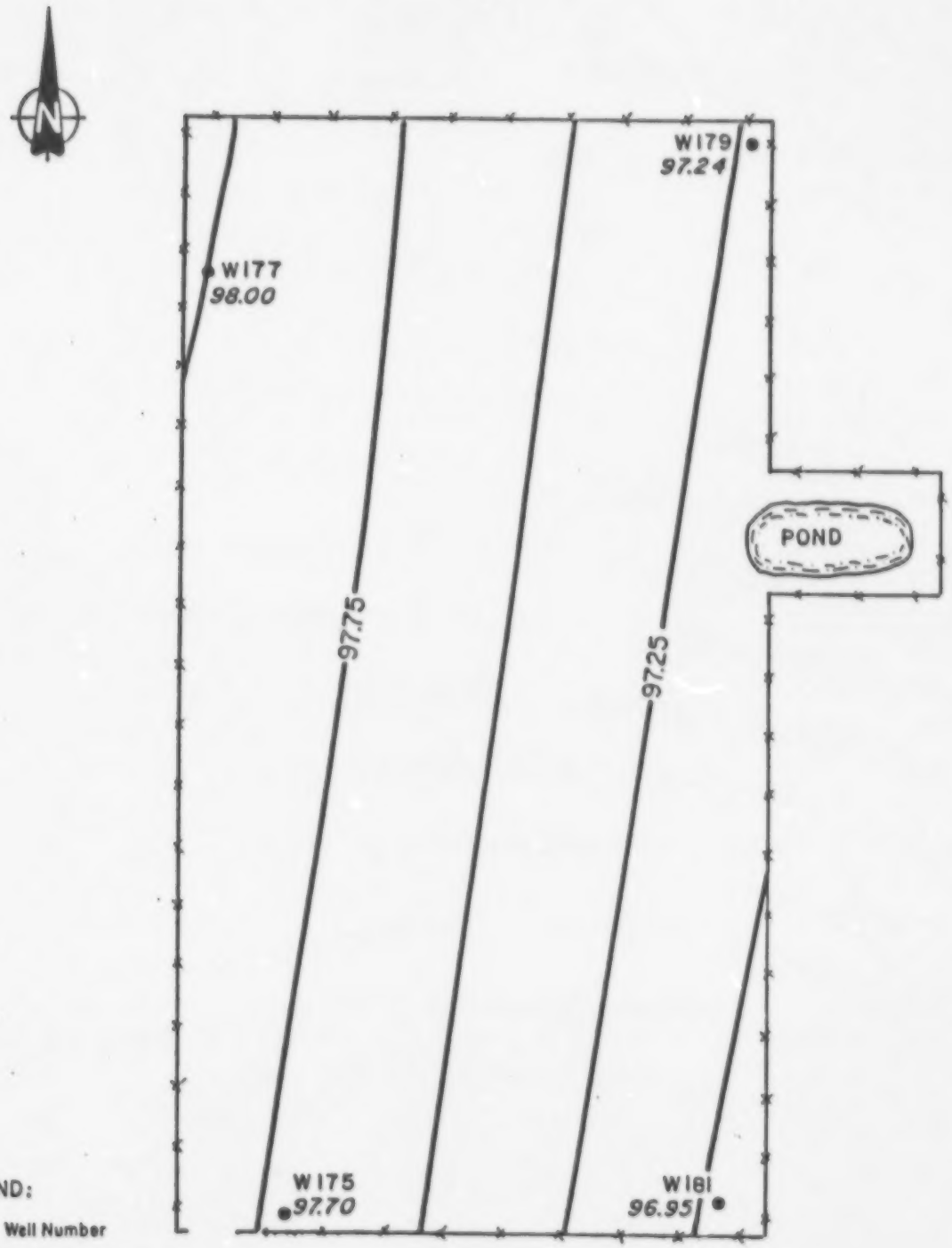


Figure 8. Water table contour map (February 19, 1987).

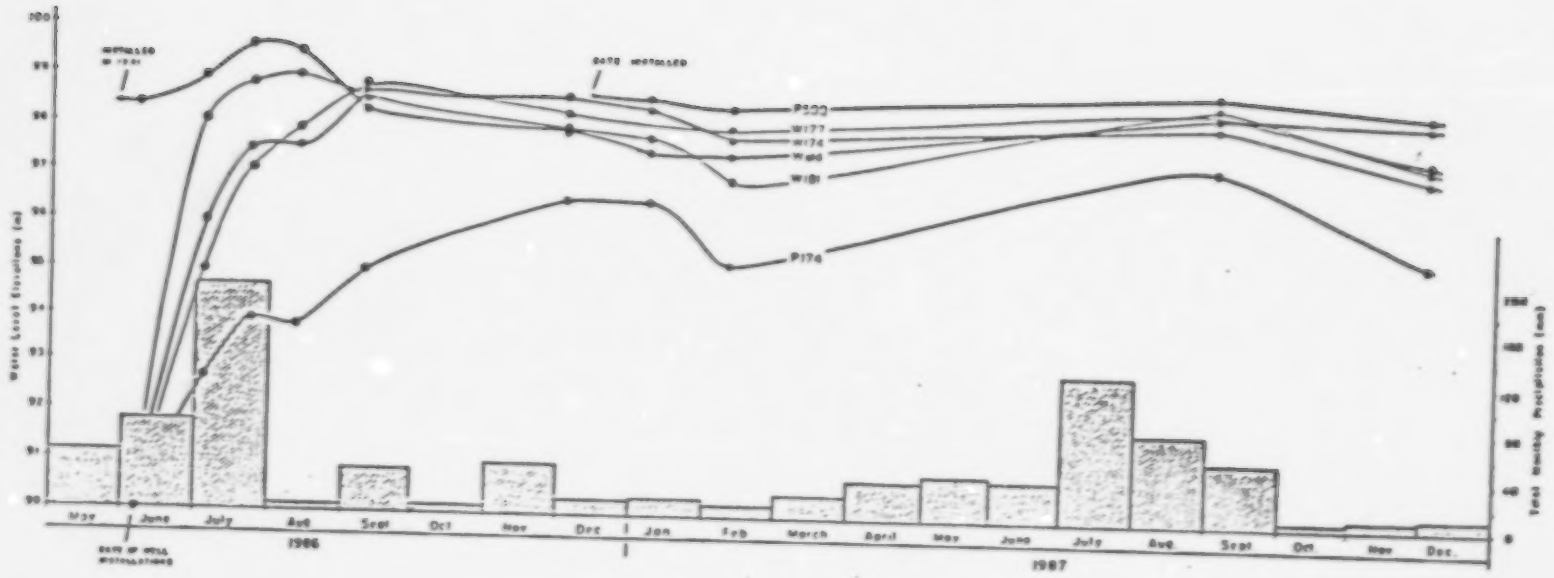


Figure 9. Water level fluctuations versus precipitation.

7.4 CHEMISTRY

7.4.1 Groundwater Chemistry

Groundwater samples were collected from chemical analysis on September 11, and December 3, 1986, and on January 6, September 2, and December 1, 1987. Prior to sampling, monitors were properly purged to ensure samples were representative of formation water. Samples were collected using a peristaltic pump and filtered in the field using a 0.45 mm filter. A list of parameters analyzed, and preservation techniques used, is attached. Samples were analyzed by the Alberta Environment laboratories in Lethbridge and Vegreville.

Analytical data (Appendix) indicate that shallow groundwater chemistry is highly variable, reflecting the complex mineralogy of the till. To a depth of approximately 6 m, groundwater varies from the calcium/magnesium - bicarbonate to the calcium/magnesium - sulphate type. The total dissolved solids concentration (TDS) varies from 480 - 7000 mg/L, with a mean of 3000 mg/L. Groundwater from the piezometers completed at the 9 m depth is the calcium/magnesium - sulphate type with a TDS concentration varying from 2500 - 4100 mg/L.

Total organic carbon (TOC) concentrations in groundwater very from 10 to 50 mg/L, with a mean of 25 mg/L. This indicates that groundwater has a relatively low organic load.

Detailed information about shallow groundwater chemistry prior to establishment of the plots is not available. However, two samples collected from a well installed prior to sludge-nutrient application were analyzed for key indicators of contamination (Peake et al, 1984) (Table 22). A comparison of 1986-87 analytical data to pre-sludge

Table 22. Groundwater chemistry before sludge application.

Date	TC	VOC	TOC	Cl	NO_3	SO_4	pH
82/06/22	190	53	67	3	0.1	2830	7.0
82/07/08	164	35	48	1.8	0.1	2680	7.0

application groundwater chemistry data indicates that the chloride and nitrate levels have increased substantially, suggesting groundwater contamination. The probably source of the chloride and nitrate is from the aqueous portion of the sludge and nutrients applied to the site, respectively.

The chloride ion was used to obtain information about the areal extent of groundwater contamination. Chloride is a suitable indicator because it has a low ambient concentration at the site (<10 mg/L), is relatively inert and extremely mobile in the aqueous environment. Figure 10 indicates that shallow groundwater is contaminated beneath and down gradient from the plots. Groundwater tends to be more contaminated in the eastern half of the plots, probably since this area received to application of sludge. The large amount of sludge applied to the east half of plot 8 (in the northeast corner of the demonstration plots) may account for unusually high chloride levels in groundwater from P 495 and W 179.

Groundwater contamination tends to decrease rapidly with depth (Figure 11a,b). This reflects the strong attenuation capacity of the surficial materials. Numerous biological, physical and chemical processes are important in retarding the movement of contaminants from the site. Considerable variation of the chloride concentration was detected in 1987 groundwater samples. The shallow wells in the north eastern part of the site showed the greatest variation, with chloride concentration highest during the September event (Figure 11b). These variations are throught to be due to the flushing action of the groundwater recharge during the high summer rainfall. Since groundwater movement is highly variable in the complex till structure of area, the wells throughout the site are affected to different extents.

In general, shallow groundwater is of poor quality with several parameters exceeding upper limits established in Canadian Drinking water standards (C.D.W.S.) (Health and Welfare Canada, 1976; Appendix). It is interesting to note that the lead concentration in groundwater exceeded the C.D.W.S. in almost every analysis. It is uncertain whether this is a natural occurrence or attributable to contamination. Since the concentration of other metals, with the

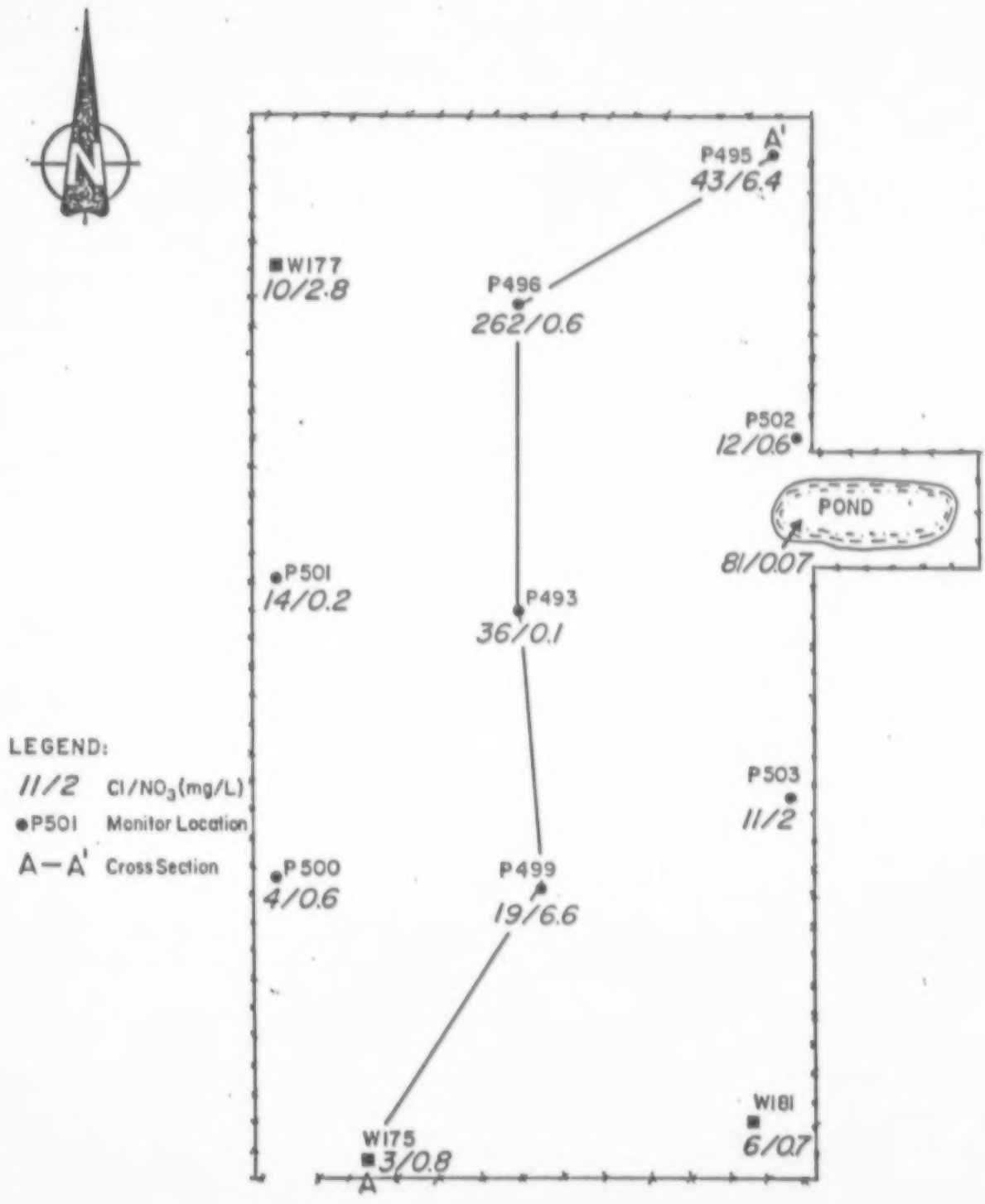


Figure 10 Areal distribution of chloride and nitrate concentrations (January 6, 1987).

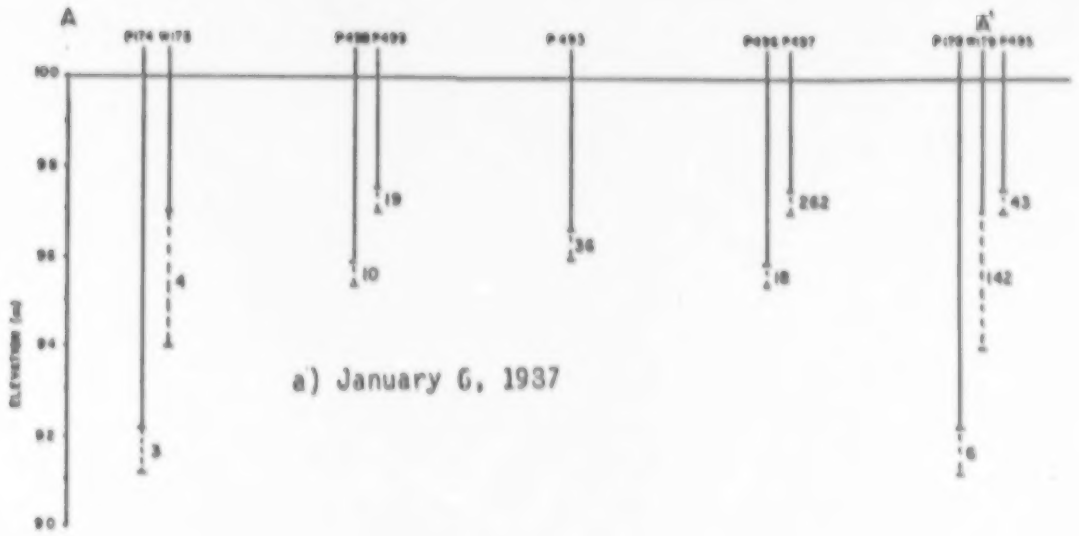


Figure 11a. Chloride concentration variation with depth along section A-A'. January 6, 1987.

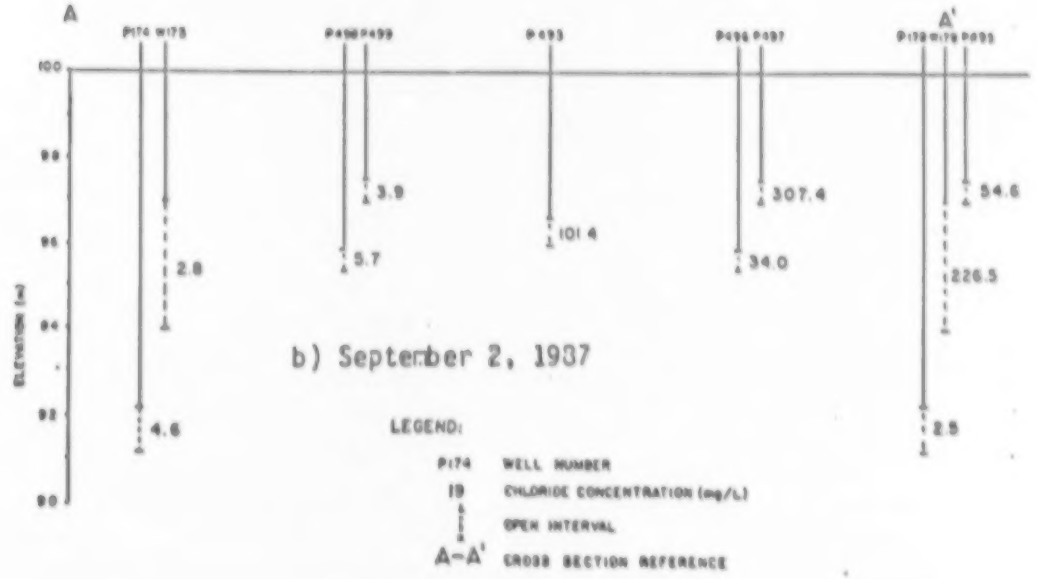


Figure 11b. Chloride concentration variation with depth along section A-A'. September 2, 1987.

exception of manganese levels which are commonly high in groundwater from till, are significantly below C.D.W.S., suggests that contamination is not the source of the elevated lead levels.

7.4.2 Surface Water Chemistry

A sample collected from the runoff pond, prior to sludge application in 1982, was analyzed for key indicators of contamination. The analysis (Table 23) indicates that the water had a very low organic and inorganic load. Immediately after application of the sludge and nutrients, the concentrations of chloride, nitrate and sulphate increased dramatically (Figure 12). The analysis of a pond water sample collected on November 4, 1986 and September 2, 1987 indicates that the concentration of chloride, nitrate and sulphate have decreased since the last sludge-nutrient application in 1983, but are still above background levels.

Table 23. Analysis of pond water prior to sludge application.

Date	TC	VOC	TOC	Cl	NO_3	SO_4	pH
82/07/08	30	0.9	17	1	4.6	3.2	7.4

From Peake, et al. 1983.

7.5 CONCLUSIONS

The demonstration plots are underlain by relatively low permeability silty clay till to a depth of at least 9 m. Fractures were detected in the till to a depth of approximately 2.5 m.

The predominant direction of shallow groundwater flow is to the east-northeast. Depth to water table at the site averages 2.5 m. Monitor response time to water table fluctuation varies considerably, with depth.

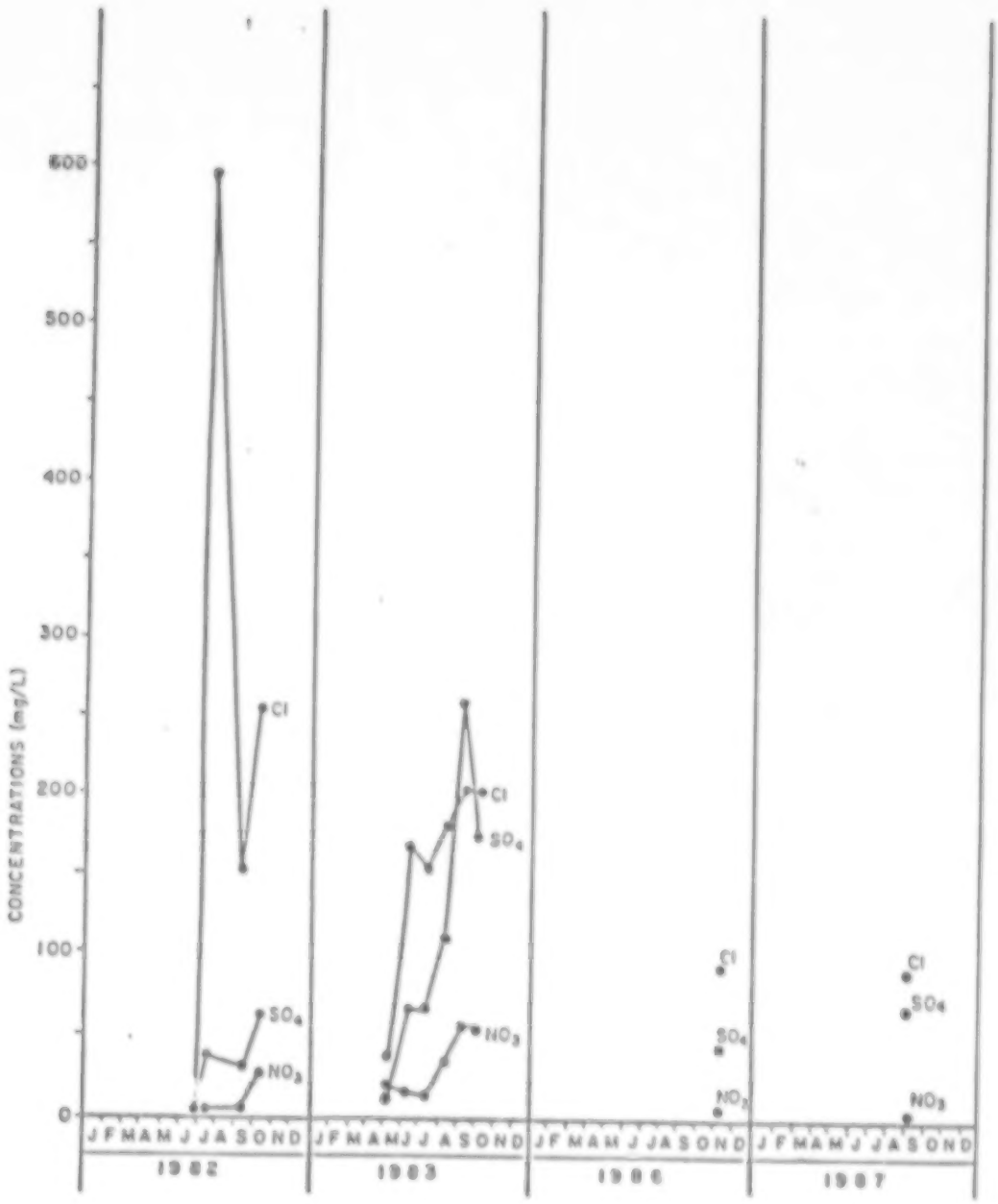

CONCENTRATIONS (mg/L)
600
500
400
300
200
100
0
Cl
SO4
NO3
J F M A M J J A S O N D J F M A M J J A S O N D J F M A M J J A S O N D J F M A M J J A S O N D
1982
1983
1986
1987

Figure 12. Chloride, nitrate, and sulphate concentration variations in pond water.

Shallow groundwater beneath and down gradient from the plots is contaminated, primarily with inorganic constituents. The contamination decreases rapidly with depth. Water in the surface runoff pond is also contaminated. Contaminant concentrations in surface water increases rapidly after precipitation events.

7.6 FUTURE WORK

As the well installation work at the site is complete, only monitoring activities are planned:

- single well response tests will be conducted to obtain detailed hydraulic conductivity information. The data will be used to estimate groundwater flow rates;
- water level monitoring will continue;
- an attempt will be made to collect groundwater and surface water samples for analysis every three months;
- groundwater samples for detailed organic analysis will be collected from the two stainless steel monitors.

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9. APPENDICES

9.1 BOREHOLE LITHOLOGY
9.2 CORE DESCRIPTION
9.3 MONITOR COMPLETION DETAILS
9.4 LIST OF PARAMETERS ANALYZED AND PRESERVATION TECHNIQUES
9.5 GROUNDWATER CHEMISTRY ANALYSES

APPENDIX 9.1

BOREHOLE LITHOLOGY

GROUNDWATER PROTECTION BRANCH DRILL HOLE LOG

Land Location SE Sec. 10 Tp. 50 R. 1 W. 4

Date June 4, 1986 Supervisor Ceroici/deBrentani

Project Lloydminster Oil Sludge Plots (Land Farming)

Test Hole 174 to 181 inclusive.

Test Hole 174

DEPTH (m)	DEPOSIT	DESCRIPTION	M.C.::
0.0 - 4.0	till	sandy to silty clay, brown, dense, some pebbles	d
4.0 - 6.0	till	sandy to silty clay, grey, some small pebbles	sm
6.0 - 7.5	till	sandy to silty clay, grey, very dense, some iron oxide staining	m
7.5 - 9.0	till	sandy to silty clay, grey, very dense, some thin, fine grained sand lenses	m
TH 175			
0.0 - 6.0	same as #174		
TH 176			
0.0 - 3.0	till	sandy to silty clay, brown, dense, some pebbles, thin sand lenses, fractures containing calcium compounds, some iron oxide staining	sm
3.0 - 4.0	till	sandy to silty clay, brown, very dense	sm
4.0 - 8.0	till	sandy to silty clay, grey, very dense	sm
TH 177			
0.0 - 6.0	same as #176		

::Moisture Content: d(dry); sm(slightly moist); m(moist); vm(very moist); s(saturated)

#416

DEPTH (m)	DEPOSIT	DESCRIPTION	M.C.*
TH 178			
0.0 - 4.0	till	sandy to silty clay, brown, dense, some pebbles, iron oxide staining, fractures containing calcium compounds	d
4.0 - 6.0	till	sandy to silty clay, grey, dense	sm
6.0 - 9.0	till	sandy to silty clay, grey, dense, thin fine grained sand layers, iron oxide stains	s
TH 179			
0.0 - 6.0	same as #178		
TH 180			
0.0 - 3.0	till	sandy to silty clay, brown, slightly pliable, some snad lenses and pebbles	sm
3.0 - 7.0	till	sandy to silty clay, grey brown, dense, some thin sand layers	sm
7.0 - 7.5	sand	fine grained, brown	m
7.5 - 9.0	till	silty clay, grey, pliable	s
TH 181			
0.0 - 6.0	same as #180		

*Moisture Content: d(dry); sm(slightly moist); m(moist); vm(very moist); s(saturated)

GROUNDWATER PROTECTION BRANCH DRILL HOLE LOG

Land Location SE Sec. 10 Tp. 50 R. 1 W 4

Date December 3, 1986 Supervisor Ceroici/de Brentani

Project Lloydminster Land Treatment Study

Test Hole 493 to 503 inclusive.

Test Hole 493

DEPTH (m)	DEPOSIT	DESCRIPTION	M.C.*
0 - .2	topsoil	dark brown, loose, hydro carbons, some veg. materials	m
.2 - 1.5	till	silty clay, light brown, plastic some pebbles	m
1.5 - 2	till	silty clay, light brown, plastic iron stains, calcite fractures	m
2 - 4	till	silty clay, grey brown, crumbly, calcite fractures, thin fine grained sand streaks	m
TH 494			
0 - .2	topsoil	dark brown, loose, hydrocarbons	m
.2 - 1.5	till	sandy to silty clay, light brown, some weathering, pebbles	m
1.5 - 4.6	till	sandy to silty clay, dark brown, pebbles	m
TH 495			
0 - 3	same as TH 494		
TH 496			
0 - .1	topsoil	dark brown, clayey	sm
.1 - 1.2	till	sandy clay, light brown, firm coarse sand and pebbles	sm
1.2 - 3	till	silty clay, grey brown, firm, pebbles	sm
3 - 4.5	till	silty clay, darker, firm, pebbles	sm

*M.C. (Moisture Content): d(dry); sm(slightly moist); m(moist); vm(very moist); s(saturated)

#416

DEPTH (m)	DEPOSIT	DESCRIPTION	M.C.*
TH 497			
0 - 3	same as TH 496		
TH 498			
0 - 1.5	till	silty clay, brown, firm, some calcite streaks, small pebbles	sm
1.5 - 3	till	silty clay, darker, firm, pebbles	sm
3 - 4.5	till	silty clay, grey brown, firm, some pebbles and stones	m
TH 499	same as TH 498		
TH 500			
0 - 1.5	till	silty clay, dark brown, firm calcite streaks, pebbles	sm
1.5 - 3.7	till	silty clay, dark brown, firm, few pebbles	m
3.7 - 4.3	sand	silty-fine grained, light brown	s
TH 501			
0 - .5	till	silty clay, brown, firm	sm
.5 - 1.5	till	silty clay, dark brown, firm, calcite streaks	sm
1.5 - 4.3	till	silty clay, dark brown, firm, some pebbles	m
TH 502			
0 - 1	till	silty clay, dark brown, firm, some pebbles	sm
1 - 1.5	till	silty clay, dark brown, firm, calcite streaks	sm
1.5 - 4.3	till	silty clay, dark brown, firm, some pebbles	m

*M.C. (Moisture Content): d(dry); sm(slightly moist); m(moist); vm(very moist); s(saturated)

#416

DEPTH (m)	DEPOSIT	DESCRIPTION	M.C.*
TH 503			
0 - 1	till	sandy clay, dark brown, firm	sm
1 - 1.5	till	silty clay, grey brown, firm, calcite streaks	sm
1.5 - 4.3	till	silty clay, grey brown, firm, few pebbles	sm

*M.C. (Moisture Content): d(dry); sm(slightly moist); m(moist); vm(very moist); s(saturated)

#416

GROUNDWATER PROTECTION BRANCH DRILL HOLE LOG

Land Location SE Sec. 10 Tp. 50 R. 1 W 4

Date September 2, 1987 Supervisor Ceroici/de Brentani

Project Lloydminster Land Treatment Study

Test Hole 331 to 332 inclusive.

Test Hole 331

DEPTH (m)	DEPOSIT	DESCRIPTION	M.C.*
0 - .2	topsoil	dark brown, loose, hydro carbons, some veg. materials	m
.2 - 1.5	till	silty clay, light brown, plastic some pebbles	m
1.5 - 2.0	till	silty clay, light brown, plastic, iron oxide stains and fractures with calcite	m
2 - 5.4	till	silty clay, grey brown, crumbly, fine grained sand streaks sand streaks	m
TH 332			
0 - .2	topsoil	dark brown, loose	sm
.2 - 4.0	till	sandy to silty clay, brown, some pebbles, dense, fractures with calcite and iron oxide stains	m
4.0 - 5.0	till	silty clay, grey, dense	m

*M.C. (Moisture Content): d(dry); sm(slightly moist); m(moist); vm(very moist); s(saturated)

#416

APPENDIX 9.2

CORE DESCRIPTION

Core Description Test Hole #493

DEPTH (m)	DESCRIPTION
0-0.15	soil, clayey, black, hydrocarbon staining, some roots
0.15-0.46	clay, brown, compact, contains pebbles
0.46-1.10	till, clayey, brown, very dense, plastic, some pebbles, iron stain streaks
1.10-1.52	till, clayey, brown, very dense, plastic, pebbles, fractures visible, calcite on fracture faces (acid test-positive)
1.52-1.83	till, clayey, brown, plastic, pebbles, calcite and iron staining on fracture faces
1.83-2.44	till, clayey, brown-grey, pebbles, less plastic, fewer fractures
2.44-3.05	till, clayey, brown-grey, pebbles, crumbly, contains fine grained sand lenses about 5 mm thick
3.50-4.12	till, clayey, brown-grey, pebbles (some coal specks), very dense, plastic, iron stain streaks

APPENDIX 9.3

MONITOR COMPLETION DETAILS

MONITORING WELL COMPLETION INFORMATION

Well Number	Date Installed	Well Depth (m)	Height of pipe above ground surface (m)	screened interval (m)	ground elevation (m)	elevation of pipe (m)
P 174	June 4/86	8.8	.87	1	100.25	101.12
W 175	June 4/86	6.0	.97	3	100.18	101.15
P 176	June 14/86	9.0	.93	1	100.30	101.23
W 177	June 4/86	6.0	1.03	3	100.30	101.33
P 178	June 4/86	8.8	.97	1	100.04	101.01
W 179	June 4/86	6.0	1.01	3	100.01	101.02
W 180	June 4/86	8.8	.97	1	100.21	101.18
W 181	June 4/86	6.0	1.02	3	100.09	101.11
P 493	Dec. 3/86	4.0	1.05	.62	100.13	101.18
P 494	Dec. 3/86	4.6	.95	.50	99.94	100.89
P 495	Dec. 3/86	3.0	1.05	.50	99.91	100.96
P 496	Dec. 3/86	4.6	1.05	.50	100.27	101.32
P 497	Dec. 3/86	3.0	1.05	.50	100.24	101.29
P 498	Dec. 3/86	4.6	1.02	.50	100.27	101.29
P 499	Dec. 3/86	3.0	.98	.50	100.26	101.24
P 500	Dec. 3/86	4.3	1.10	.50	100.10	101.20
P 501	Dec. 3/86	4.3	1.05	.50	100.08	101.13
P 502	Dec. 3/86	4.3	1.05	.50	100.05	101.10
P 503	Dec. 3/86	4.3	1.04	.50	100.23	101.27
Old Well	1983	11.0	.93	?	100.00	100.93
W 331	Sept. 2/87	5.4	.65	.50	100.05	100.70
W 332	Sept. 2/87	5.0	.45	.50	100.02	100.47

APPENDIX 9.4

LIST OF PARAMETERS ANALYZED AND PRESERVATION TECHNIQUES

List of Chemical Parameters and Preservation Techniques.

Chemical Parameter	Method of Preservation
Inorganic	
Cl, SO_4, HCO_3, NH_4,	- 250 ml plastic bottle
Na, K, Ca, Mg	- refrigerate
Organic	
COD	- 125 ml plastic bottle
	- acidify 5 ml H_2SO_4
	- refrigerate
TOC	- 125 ml plastic bottle
	- refrigerate
Metals	
Cu, Fe, Mn, Pb, Zn	- 125 ml plastic bottle
	- acidify 5 ml (1:1) HNO_3
	- refrigerate

APPENDIX 9.5

GROUNDWATER CHEMISTRY ANALYSES

GROUNDWATER CHEMISTRY LLOYDMINSTER
September 10,1986

	C.D.W.S.	WELL NUMBER							
		P 174	W 175	P 176	W 177	P 178	W 179	P 180	W 181	W old
Lab Data										
pH		7.67	8.04	7.70	7.91	7.68	7.95	7.83	8.03	7.85
E.C. (mS/cm)		2.96	0.95	4.35	5.50	2.87	1.40	3.84	2.85	3.30
S.A.R.		0.53	0.34	1.63	2.17	0.63	0.48	1.80	0.56	1.63
Lab Analysis - all parameters in mg/l										
T.H.	500	2075.00	560.00	2925.00	3550.00	1975.00	855.00	2455.00	1990.00	1450.00
Ca	N.E.	504.00	135.00	570.00	420.00	458.00	180.00	552.00	468.00	314.00
Mg	150	198.05	53.46	364.50	607.50	201.69	98.41	261.23	199.26	161.60
K	N.E.	12.51	5.87	15.64	15.25	10.95	4.30	13.69	8.21	3.91
Na	500	55.20	18.40	202.40	296.70	64.40	32.20	204.70	57.50	142.60
NH4-N	0.5	1.12	0.07	1.47	0.28	2.38	0.07	0.84	0.35	0.14
NO3-N + NO2-N	10	0.07	3.36	0.14	6.65	0.07	2.87	0.07	7.00	11.62
Cl	250	4.61	3.55	8.15	12.41	2.13	257.01	11.70	4.61	815.35
SO4	500	1584.00	96.00	2736.00	3648.00	1560.00	196.80	2184.00	1584.00	141.60
CO3	N.E.	-	-	-	-	-	-	-	-	-
HCO3	N.E.	600.85	568.52	534.36	580.72	570.96	416.63	636.23	461.16	459.94
T.A.	500	493.00	466.00	438.00	476.00	468.00	342.00	522.00	378.00	377.00
T.D.S.	1000	2655.00	607.00	4162.00	476.00	2580.00	987.00	3541.00	2580.00	1857.00
Organic Indicators										
C.O.D.		160.00	15.00	116.00	144.00	29.00	87.00	128.00	49.00	221.00
T.O.C.		-	-	-	-	-	-	-	-	-
Metals										
Fe	0.3	0.13	0.10	0.22	0.14	0.12	0.09	0.12	0.11	0.23
Mn	0.05	1.63	0.02	2.90	0.08	0.22	0.01	0.18	0.02	0.78
Cu	1.0	0.02	0.01	0.02	0.03	0.02	0.01	0.02	0.02	0.02
Zn	5.0	0.04	0.02	0.04	0.03	0.04	0.02	0.03	0.03	0.03
Pb	0.05	0.16	0.12	0.19	0.20	0.17	0.13	0.13	0.17	0.18

N.E. - Not Established
C.D.W.S. - Canadian Drinking Water Standards

GROUNDWATER CHEMISTRY LLOYDMINSTER
December 3,1986

	C.D.W.S.	WELL NUMBER								
		P 174	W 175	P 176	W 177	P 178	W 179	P 180	W 181	W old
Lab Data										
pH		7.01	7.53	7.09	7.43	7.07	7.48	7.16	7.53	7.55
E.C. (mS/cm)		3.92	0.94	4.30	5.63	2.89	1.82	3.91	3.02	3.20
S.A.R.		0.60	0.30	1.70	2.20	0.70	0.60	1.80	0.60	1.40
Lab Analysis - all parameters in mg/l										
T.H.	500	2000.00	550.00	2780.00	3770.00	1925.00	940.00	2400.00	2050.50	1360.00
Ca	N.E.	498.00	131.00	542.00	516.00	440.00	204.00	542.00	472.00	276.00
Mg	150	183.47	53.46	346.28	602.64	200.47	104.49	253.94	212.62	164.03
K	N.E.	12.90	6.26	16.42	14.47	10.95	4.30	14.08	7.82	4.30
Na	500	59.80	18.40	202.40	310.50	66.70	39.10	209.30	59.80	119.60
NH4-N	0.5	1.75	0.07	2.87	0.21	1.12	0.07	3.43	0.14	0.14
NO3-N + NO2-N	10	0.07	2.80	0.07	5.04	0.07	5.18	0.07	4.76	14.70
Cl	250	2.84	3.55	8.15	10.63	3.55	230.43	11.70	4.61	744.45
SO4	500	1536.00	108.00	2736.00	3744.00	1536.00	302.40	2256.00	1704.00	134.40
CO3	N.E.	-	-	-	-	-	-	-	-	-
HCO3	N.E.	640.50	566.08	517.28	629.52	576.45	447.13	644.16	497.15	466.65
T.A.	500	525.00	464.00	424.00	516.00	472.00	366.00	528.00	408.00	382.00
T.D.S.	1000	2610.00	612.00	4110.00	5530.00	2540.00	1130.00	3610.00	2730.00	1740.00
Organic Indicators										
C.O.D.		-	-	-	-	-	-	-	-	-
T.O.C.		-	-	-	-	-	-	-	-	-
Metals										
Fe	0.3	0.08	0.04	0.21	0.08	0.20	0.08	0.41	0.07	0.28
Mn	0.05	-	-	-	-	-	-	-	-	-
Cu	1.0	-	-	-	-	-	-	-	-	-
Zn	5.0	-	-	-	-	-	-	-	-	-
Pb	0.05	-	-	-	-	-	-	-	-	-

N.E. - Not Established
C.D.W.S. - Canadian Drinking Water Standards

GROUNDWATER CHEMISTRY LLOYDMINSTER
January 6,1987

	C.D.W.S.	WELL NUMBER																			
Lab Data		W old	P 174	W 175	P 176	W 177	P 178	W 179	P 180	W 181	P 493	P 494	P 495	P 496	P 497	P 498	P 499	P 500	P 501	P 502	P 503
pH		7.50	7.05	6.92	7.12	7.49	7.31	7.30	7.63	7.64	7.68	7.72	7.82	Y.91	7.99	8.00	8.20	8.13	7.89	7.68	7.80
E.C. (mS/cm)		3.30	2.70	1.41	4.60	5.31	2.79	1.90	3.62	3.17	1.43	3.03	1.60	4.02	6.49	1.17	0.60	2.14	4.09	3.04	0.96
S.A.R.		1.00	0.60	0.30	1.40	2.20	0.70	0.07	1.80	0.80	1.00	0.80	0.70	2.80	2.90	0.40	0.40	1.10	1.30	0.60	0.60
Lab Analysis - all parameters in mg/l																					
T.H.	500	1100.00	1975.00	940.00	2800.00	3225.00	2000.00	1125.00	2425.00	2350.00	925.00	2125.00	1075.00	3000.00	4500.00	700.00	345.00	1300.00	3000.00	2250.00	940.00
Ca	N.E.	220.00	480.00	252.00	560.00	498.00	470.00	250.00	550.00	530.00	210.00	510.00	230.00	500.00	560.00	180.00	75.00	250.00	500.00	540.00	136.00
Mg	150	133.65	188.33	75.94	352.35	402.44	200.47	121.50	255.15	249.08	97.20	206.55	121.50	425.25	793.38	60.75	30.27	144.03	425.25	218.70	48.60
K	N.E.	4.30	12.90	7.82	16.03	14.08	11.34	6.26	14.47	11.34	7.82	10.17	5.08	15.44	10.95	7.43	4.30	6.65	12.91	10.56	5.67
Na	500	73.60	57.50	23.00	200.10	303.60	69.00	92.90	204.70	89.70	66.70	85.10	95.20	350.80	450.80	23.00	18.40	92.00	163.30	69.00	29.90
NH4-N	0.5	0.14	1.89	0.14	2.17	0.28	0.77	0.14	4.20	0.21	4.90	2.80	3.29	2.24	2.45	1.54	2.87	0.28	3.01	0.91	1.89
NO3-N + NO2-N	10	17.57	0.07	0.84	0.07	6.55	0.07	9.04	0.07	0.70	0.07	0.21	6.44	0.63	18.76	0.21	6.58	2.80	0.21	0.63	1.89
Cl	250	496.30	3.55	2.84	6.38	9.93	6.38	141.80	12.41	6.38	36.51	15.24	43.60	17.73	261.43	9.93	18.79	3.55	14.18	11.70	10.63
SO4	500	112.80	1478.40	475.20	2620.80	3600.00	1632.00	576.00	2280.00	2035.20	443.20	2006.40	806.40	3312.00	4492.80	480.80	40.80	835.60	2865.60	2102.40	288.00
CO3	N.E.	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
HCO3	N.E.	805.69	642.94	592.92	564.88	63074.00	583.16	508.74	667.95	517.28	739.32	320.25	327.57	302.47	516.06	480.16	274.56	725.29	488.09	270.23	273.93
T.A.	500	414.00	527.00	486.00	463.00	517.00	478.00	417.00	530.00	424.00	606.00	262.00	268.00	314.00	423.00	328.00	307.00	594.00	334.00	222.00	306.00
T.D.S.	1000	1370.00	2540.00	1130.00	4020.00	5360.00	2680.00	1420.00	3640.00	3180.00	1250.00	3000.00	1460.00	4820.00	6870.00	881.00	413.00	1710.00	4190.00	3093.00	714.00
Organic Indicators																					
C.O.D.		-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
T.O.C.		-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Metals																					
Fe	0.3	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Mn	0.05	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Cu	1.0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Zn	5.0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Pb	0.05	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

N.E. - Not Established
C.D.W.S. - Canadian Drinking Water Standards

GROUNDWATER CHEMISTRY LLOYDMINSTER
April 14,1987

	C.D.W.S.	P 174	W 175	P 176	W 177	P 178	P 179	P 180	W 181	P 493	P 494	P 495	P 496	P 497	P 498	P 499	P 500	P 501	P 502	P 503	OLD W
Lab Data																					
pH		7.47	7.65	7.59	7.63	7.66	7.96	7.32	8.03	8.14	8.01	8.15	8.10	8.17	7.94	8.30	8.16	8.17	8.20	8.10	7.47
E.C. (mS/cm)		2.92	1.02	4.31	5.37	2.94	1.59	3.68	2.89	1.48	3.00	1.68	5.12	6.72	1.13	0.86	2.25	4.90	3.50	1.23	2.22
S.A.R.		0.50	0.20	1.70	2.10	0.60	0.50	1.80	0.60	0.80	0.80	0.06	2.60	3.00	0.30	0.40	1.20	1.70	0.60	0.60	0.70
Lab Analysis - all parameters in mg/l																					
T.H.	500	1955.00	580.00	2775.00	3700.00	1890.00	790.00	2300.00	1900.00	900.00	1930.00	930.00	3675.00	4460.00	590.00	445.00	1270.00	3370.00	1975.00	670.00	1080.00
Ca	N.E.	470.00	130.00	486.00	480.00	412.00	159.00	504.05	400.00	196.00	438.00	174.00	450.00	468.00	147.00	91.00	218.00	518.00	360.00	154.00	198.00
Mg	150	189.54	62.57	379.08	607.50	206.98	94.77	252.72	218.70	99.02	200.47	118.46	473.85	799.47	54.07	52.85	177.39	504.23	164.03	69.26	140.94
K	N.E.	12.12	4.30	15.64	13.29	10.95	2.35	13.29	6.65	5.87	8.60	2.35	14.08	10.56	4.30	2.74	6.26	10.95	6.65	5.08	3.52
Na	500	55.20	13.80	209.30	299.00	64.40	32.20	193.20	62.10	55.20	75.90	43.70	358.80	455.40	18.40	18.40	96.60	232.30	92.90	25.30	55.20
NH4-N	0.5	3.50	0.07	1.96	0.28	1.68	0.07	2.10	0.28	2.73	2.73	2.59	3.43	5.81	3.22	2.73	1.05	3.71	2.80	2.66	0.14
NO3-N + NO2-N	10	0.14	2.87	0.07	4.90	0.21	19.60	0.07	4.06	0.49	0.70	5.39	0.14	2.24	0.21	2.87	0.84	0.14	0.21	0.07	21.00
Cl	250	3.55	2.84	8.86	8.86	11.70	228.65	9.93	4.61	26.59	9.93	67.15	11.70	233.97	7.09	8.86	2.55	11.70	18.79	7.09	350.25
SO4	500	1464.00	108.00	2572.80	5630.40	1478.40	187.20	2088.00	1848.00	345.60	1632.00	576.00	3177.60	4272.00	168.00	40.80	825.60	3129.60	1190.40	283.20	153.60
CO3	N.E.	-	-	-	-	-	-	-	-	-	-	-	-	-	-	6.2	-	-	-	-	-
HCO3	N.E.	637.45	599.63	572.18	607.56	562.42	385.78	622.20	517.89	739.93	662.38	601.38	530.09	676.05	563.64	530.85	736.44	605.72	514.84	510.84	530.63
T.A.	500	522.90	492.00	469.80	498.00	461.00	320.00	510.00	424.00	606.00	379.00	329.00	434.00	575.00	462.00	450.00	602.00	496.00	422.00	422.00	442.00
T.D.S.	1000	2510.00	639.00	3960.00	5370.00	2670.00	920.00	3370.00	2480.00	1100.00	2600.00	1190.00	4750.00	6600.00	681.00	501.00	1690.00	4700.00	2050.00	801.00	1260.00
Organic Indicators																					
C.O.D.		-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
T.O.C.		-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Metals																					
Fe	0.3	0.10	0.05	0.20	-	0.57	0.03	0.74	0.08	1.05	0.35	0.07	0.55	0.13	0.57	1.30	0.05	0.03	0.31	0.05	0.05
Mn	0.05	1.00	0.06	4.20	0.31	1.49	0.01	2.37	0.05	2.63	3.03	0.30	7.00	4.05	2.10	1.71	0.12	7.13	1.73	2.20	0.26
Cu	1.0	0.01	0.01	0.03	0.03	0.01	0.01	0.02	0.03	0.01	0.02	0.01	0.02	0.03	0.01	0.01	0.01	0.02	0.01	0.01	0.01
Zn	5.0	0.01	0.01	0.03	0.03	0.02	0.01	0.01	0.01	0.01	0.01	0.02	0.02	0.03	0.02	0.01	0.03	0.01	0.01	0.01	0.01
Pb	0.05	0.08	0.03	0.10	0.11	0.09	0.04	0.11	0.08	0.03	0.09	0.04	0.11	0.13	0.04	0.03	0.06	0.11	0.07	0.04	0.06

N.E. - Not Established
C.D.W.S. - Canadian Drinking Water Standards

GROUNDWATER CHEMISTRY LOYDMINSTER
September 2,1987

	C.D.W.S.	WELL NUMBER																			
Lab Data		P 174	W 175	P 176	W 177	P 178	W 179	P 180	W 181	P 493	P 494	P 495	P 496	P 497	P 498	P 499	P 500	P 501	P 502	P 503	Pond	W old
pH		7.57	7.90	7.51	7.87	7.71	7.90	7.84	7.47	7.88	7.42	7.68	7.36	7.38	8.02	7.74	7.33	7.44	7.40	7.60	6.81	7.26
E.C. (mS/cm)		2.88	1.06	4.46	5.53	3.17	1.86	3.98	2.00	1.70	3.88	1.78	1.33	5.51	0.77	6.57	2.41	5.16	2.44	1.42	0.60	3.33
S.A.R.		0.54	0.34	1.78	2.21	0.74	0.53	1.87	0.50	0.97	0.76	0.65	0.34	2.99	0.36	2.78	1.28	2.31	0.64	0.52	1.81	1.60
Lab Analysis - all parameters in mg/l																						
T.H.	500	1836.50	540.00	3740.00	3450.00	2005.00	910.00	3310.00	1135.00	780.00	1750.00	955.00	705.00	3110.00	379.00	3930.00	1240.00	3080.00	1305.00	720.00	148.50	1455.00
Ca	N.E.	424.00	120.00	450.00	440.00	424.00	181.00	490.00	240.00	157.00	402.00	174.00	154.80	424.00	70.80	440.00	196.00	400.00	300.00	143.00	39.80	260.00
Mg	150	188.33	62.49	387.58	571.05	239.63	110.56	263.65	131.22	94.16	181.03	126.36	76.91	498.15	49.09	687.69	182.25	505.44	154.31	88.09	11.91	195.62
K	N.E.	11.34	3.91	14.86	12.12	10.95	2.74	12.90	4.30	4.69	7.04	1.56	4.30	13.29	2.74	8.99	4.28	11.34	5.47	5.47	3.91	4.30
Na	500	52.90	18.40	213.90	299.00	75.90	38.87	207.00	39.10	62.10	73.60	46.00	20.70	384.10	16.10	480.20	103.50	282.90	55.20	32.20	50.60	140.30
NH4-N	0.5	2.73	0.14	2.10	0.28	1.75	0.07	2.52	0.14	9.87	4.06	0.91	2.87	2.87	2.52	3.92	3.64	2.45	4.41	2.03	0.14	0.35
NO3-N + NO2-N	10	0.14	3.08	0.35	6.49	0.07	2.52	0.14	3.85	0.42	0.42	5.46	0.28	1.33	1.75	12.95	0.07	0.07	0.07	0.07	0.07	8.02
Cl	250	4.61	2.84	7.09	9.22	2.48	226.53	10.28	3.90	101.39	14.18	54.59	3.90	34.03	5.67	307.25	3.19	10.62	26.59	6.74	82.60	588.47
SO4	500	1367.20	123.36	2707.20	3942.40	1665.60	275.52	2208.00	912.00	249.12	1440.00	576.00	229.44	3360.60	70.56	3580.80	883.20	3072.00	1075.20	335.52	77.76	476.64
CO3	N.E.	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
HCO3	N.E.	639.38	570.96	567.91	602.68	574.01	439.20	608.17	334.89	676.49	478.85	426.39	649.65	552.05	427.61	595.97	740.54	687.47	478.85	583.77	78.69	489.83
T.A.	500	524.00	468.00	464.00	494.00	471.00	360.00	499.00	275.00	555.00	393.00	350.00	533.00	453.00	351.00	489.00	607.00	564.00	393.00	479.00	65.00	402.00
T.D.S.	1000	2387.00	626.00	4073.00	5192.00	2693.00	1061.00	3495.00	1513.00	1016.00	2361.00	1214.00	815.00	4976.00	436.00	5781.00	1744.00	4624.00	1858.00	901.00	305.00	1946.00
Organic Indicators																						
C.O.D.		25.00	5.00	80.00	130.00	30.00	50.00	35.00	25.00	215.00	100.00	75.00	75.00	180.00	70.00	215.00	95.00	205.00	60.00	45.00	180.00	175.00
T.O.C.		11.00	5.00	26.00	54.00	9.00	13.00	9.00	10.00	39.00	29.00	29.00	-	64.00	18.00	84.00	24.00	61.00	26.00	14.00	53.00	24.00
Metals																						
Fe	0.3	0.38	0.10	0.19	0.10	0.77	0.03	0.37	0.04	0.07	0.35	0.34	0.07	0.05	0.05	1.03	0.33	0.38	0.11	0.42	0.04	0.03
Mn	0.05	1.94	0.05	4.03	0.08	1.56	0.02	2.20	0.05	1.48	1.98	0.34	2.27	5.05	0.44	1.63	0.27	4.75	0.91	2.44	0.01	0.22
Cu	1.0	0.01	0.01	0.02	0.02	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.03	0.01	0.01	0.01	0.01	0.01	0.01
In	5.0	0.02	0.02	0.03	0.05	0.02	0.01	0.02	0.02	0.01	0.03	0.03	0.01	0.02	0.02	0.03	0.01	0.01	0.02	0.01	0.01	0.01
Pb	0.05	0.09	0.05	0.12	0.12	0.11	0.08	0.08	0.05	0.03	0.07	0.04	0.03	0.11	0.04	0.13	0.06	0.12	0.07	0.06	0.04	0.07

N.E. - Not Established
C.D.W.S. - Canadian Drinking Water Standards

GROUNDWATER CHEMISTRY LLOYDMINSTER
October 4,1987

	C.D.W.S.	WELL NUMBER
		Pond
Lab Data		
pH		6.94
E.C. (mS/cm)		0.54
S.A.R.		1.90
Lab Analysis - all parameters in mg/l		
T.H.	500	160.00
Ca	N.E.	44.00
Mg	150	12.15
K	N.E.	3.52
Na	500	55.20
NH4-N	0.5	0.14
NO3-N + NO2-N	10	0.07
Cl	250	80.83
SO4	500	43.20
CO3	N.E.	-
HCO3	N.E.	151.89
T.A.	500	124.00
T.D.S.	1000	314.00
Organic Indicators		
C.O.D.		134.00
T.O.C.		-
Metals		
Fe	0.3	0.36
Mn	0.05	0.06
Cu	1.0	0.01
Zn	5.0	0.03
Pb	0.05	0.13

N.E. - Not Established
C.D.W.S. - Canadian Drinking Water Standards

GROUNDWATER CHEMISTRY LLOYDMINSTER
December 1, 1987

	C.D.W.S.	WELL NUMBER																				
		W 331	W 332	P 174	W 175	P 176	W 177	P 178	W 179	P 180	P 181	P 494	P 495	P 496	P 497	P 498	P 499	P 500	P 501	P 502	P 503	W 493	W old
Lab Data																							
pH		7.06	7.03	7.02	7.22	7.02	7.44	7.18	7.20	7.54	7.73	7.66	7.61	7.68	7.87	7.93	7.03	8.13	-	7.02	8.06	8.01	7.92
E.C. (mS/cm)		1.40	3.44	2.77	1.07	4.24	5.41	2.93	2.00	3.84	2.52	2.80	2.20	5.34	7.07	1.59	0.96	2.32	-	3.55	1.41	1.56	2.86
S.A.R.		0.79	1.15	0.54	0.42	1.69	2.19	0.67	0.72	1.67	0.60	0.95	0.73	2.98	3.67	0.60	0.25	1.38	-	0.70	0.51	1.20	0.83
Lab Analysis - all parameters in mg/l																							
T.H.	500	705.00	2360.00	1805.00	580.00	2730.00	3580.00	1890.00	1725.00	2365.00	1605.00	1790.00	1350.00	3150.00	4200.00	700.00	520.00	1260.00	-	1590.00	705.00	750.00	1305.00
Ca	N.E.	144.60	492.00	424.00	119.40	498.00	416.00	498.00	386.00	458.00	360.00	400.00	256.00	394.00	404.00	124.00	91.80	191.00	-	336.00	159.20	132.60	226.00
Mg	150	83.47	274.59	181.03	68.16	358.43	617.22	211.41	184.68	377.02	182.25	187.11	172.53	526.10	794.61	94.77	71.08	189.54	-	183.25	86.75	101.70	179.82
K	N.E.	4.30	10.56	11.73	3.91	15.25	13.69	10.95	8.21	13.29	9.87	7.82	3.92	14.86	11.73	5.47	1.96	6.65	-	7.04	5.87	4.69	2.74
NH4-N	0.5	0.20	0.43	2.81	0.13	2.42	0.24	1.25	0.20	2.53	0.20	2.03	1.79	1.38	1.51	2.97	0.81	0.63	-	2.06	1.19	0.76	0.20
NO3-N + NO2-N	10	4.14	0.31	0.07	1.41	0.06	3.78	0.07	2.76	0.11	3.95	1.75	0.10	0.15	9.07	0.07	0.11	0.31	-	0.52	0.21	0.43	17.30
Cl	250	21.27	9.22	4.61	5.32	9.93	10.99	3.99	84.14	12.05	4.25	14.53	32.26	8.15	276.51	2.84	3.55	2.84	-	26.94	6.03	20.26	627.47
SO4	500	306.26	2155.20	1377.60	139.20	2673.60	3523.20	1478.40	1228.80	2668.80	1272.00	1507.20	956.24	3369.60	4116.48	383.04	72.44	902.40	-	1147.20	304.32	290.56	96.00
CO3	N.E.	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
HCO3	N.E.	556.32	423.34	652.57	597.88	559.37	617.93	571.57	519.72	611.32	583.25	517.38	525.82	617.32	753.96	445.30	615.49	639.28	-	584.30	606.98	713.89	456.89
T.A.	500	456.00	347.00	535.00	490.00	459.00	507.00	469.00	426.00	501.00	413.00	424.00	431.00	506.00	618.00	365.00	505.00	524.00	-	479.00	498.00	585.00	375.00
T.D.S.	1000	901.00	3281.00	2367.00	659.00	4036.00	5204.00	2462.00	2231.00	3331.00	2126.00	2601.00	1739.00	5003.00	6571.00	870.00	565.00	1723.00	-	2056.00	895.00	996.00	1904.00
Organic Indicators																							
C.O.D.		60.00	52.00	26.00	20.00	76.00	136.00	10.00	44.00	24.00	20.00	76.00	116.00	156.00	236.00	66.00	56.00	56.00	192.00	92.00	62.00	66.00	92.00
T.O.C.		22.00	17.00	9.00	5.00	26.00	55.00	9.00	16.00	10.00	11.00	23.00	29.00	66.00	86.00	17.00	14.00	21.00	57.00	16.00	12.00	10.00	11.00
Metals																							
Fe	0.3	0.09	0.03	0.36	0.04	0.08	0.05	0.36	0.05	0.06	0.01	0.09	0.66	0.43	0.15	0.50	0.05	0.06	0.40	0.08	0.29	0.03	0.03
Mn	0.05	0.69	1.06	2.07	2.07	4.35	0.08	1.79	0.06	2.47	0.01	2.16	2.94	2.84	0.65	2.38	1.04	0.32	2.14	2.14	1.03	0.75	0.08
Cu	1.0	0.01	0.03	0.02	0.01	0.02	0.02	0.01	0.01	0.02	0.01	0.02	0.01	0.02	0.03	0.01	0.01	0.01	0.02	0.01	0.01	0.01	0.01
Zn	5.0	0.02	0.06	0.03	0.02	0.03	0.02	0.02	0.01	0.04	0.01	0.05	0.01	0.02	0.03	0.01	0.01	0.01	0.02	0.02	0.01	0.01	0.01
Pb	0.05	0.27	0.10	0.09	0.09	0.12	0.13	0.10	0.09	0.11	0.04	0.07	0.06	0.11	0.15	0.05	0.04	0.06	0.06	0.08	0.06	0.06	0.07

N.E. - Not Established
C.D.W.S. - Canadian Drinking Water Standards